S0032-3861(96)00503-4

Polymer Vol. 38 No. 2, pp. 371–377, 1997
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

Crystal structure and morphology of melt-crystallized poly(propylene-*stat*-ethylene) fractions

S. Laihonen and U. W. Gedde*
Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

and P.-E. Werner and M. Westdahl
Department of Structural Chemistry, Stockholm University, S-106 91 Stockholm, Sweden

and P. Jääskeläinen
Borealis Polymers OY, PO Box 330, SF-06101 Porvoo, Finland

and J. Martinez-Salazar
Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain
(Received 9 May 1995; revised 10 April 1996)

Crystallinity, crystal structure and lamellar thickness in melt-crystallized samples of poly(propylene-*stat*-ethylene) fractions with 2.7–11.0 mol% ethylene comonomer and of approximately constant tacticity were assessed by wide- and small-angle X-ray scattering, differential scanning calorimetry and infra-red spectroscopy. Most of the samples were crystallized under isothermal conditions at 373 K. In comparison with an isotactic homopolymer of polypropylene, the copolymers showed lower crystallinity, melting enthalpy and average length of 3/1 helices, a slightly larger unit cell, a longer long period and an invariant lamellar thickness. The X-ray crystallinity of the copolymers remained approximately constant with increasing ethylene content, whereas the γ-crystallinity increased and the heat of fusion decreased moderately. It is suggested that the ethylene units are partially included in the crystals, and that this causes the invariance in crystallinity and crystal thickness. The observed gradual decrease in average 3/1 helix length with increasing ethylene content as assessed by infra-red spectroscopy is in accordance with this suggestion. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(propylene-*stat*-ethylene); X-ray scattering; thermal analysis)

INTRODUCTION

Isotactic polypropylene was introduced as a consequence of the independent discovery of coordination polymerization by Ziegler and Natta in 1955, and has since then increased in importance, currently being one of the four 'commodity' polymers. Low temperature brittleness and opacity are major disadvantages of the homopolymer of isotactic polypropylene. Ethylene comonomer is introduced into isotactic polypropylene in order to improve the fracture toughness and the transparency, and to decrease the processing temperatures.

The introduction of ethylene comonomer into polypropylene leads to a decrease in crystallinity, a greater tendency for the formation of γ crystals and a depression in crystallization and melting points compared with the isotactic homopolymer[1–5]. Recently, Zimmermann[1] reported data obtained by X-ray diffraction and differential scanning calorimetry (d.s.c.), which, according to the author, suggested that the ethylene units are completely rejected from the crystal phase. Avella *et al.*[2] suggested, on the basis of a minor decrease in unit cell volume, that the ethylene units are partially incorporated in the crystals. Buisco *et al.*[3] arrived at the same conclusion on the basis of crystallinity data. The scope of our work has been to study the same problem.

This paper presents data on crystal structure, crystallinity and crystal thickness for a series of poly(propylene-*stat*-ethylene) fractions using X-ray scattering, infra-red (i.r.) spectroscopy and d.s.c. The almost invariant crystallinity and crystal thickness recorded for the samples with ethylene contents in the range from 2 to 11 mol% indicate, in the light of previous results[6–9] on polypropylenes and polyethylenes, that the ethylene units are partially included in the crystals.

EXPERIMENTAL

Materials

The fractionation was performed by a direct extraction technique using solvent/nonsolvent mixtures

---

* To whom correspondence should be addressed

at constant temperature[10–13]. Xylene/ethylene glycol monoether mixtures were used for fractionating according to ethylene content generating the so-called 'e-samples', and ethylene glycol monobutyl ether/diethylene glycol monobutyl ether mixtures for fractionating according to molar mass ('m-samples')[10–12]. It is known from earlier work by Owaga and coworkers[10–12] that the e-fractions show only a moderate polydispersity in propylene sequency length, i.e. ethylene content, whereas the m-fractions show a narrower molar mass distribution and broader distribution in ethylene content. To prevent oxidation of fractions, small amounts of antioxidant were added.

A Millipore Waters 150C ALC/GPC Gel Permeation Chromatograph (g.p.c.), calibrated with polystyrene standards and broad molar mass polypropylenes, was used for molar mass determination. Two mixed beds and one 10^6 nm TSK-Gel column were used. The instrument was operated at 408 K with 1,2,4-tricholorobenzene as eluent.

The ethylene content was determined using nuclear magnetic resonance (n.m.r.) spectroscopy from proton-decoupled nuclear overhauser enhancement (NOE)^{13}C spectra obtained in a JEOL GSX400 spectrometer operating at 100.4 MHz at 423 K. The samples were dissolved in a 9/1 mixture of 1,2,4-trichlorobenzene and hexadeuterobenzene at 383–423 K. The ethylene content and sequence distributions were determined according to the method of Randall[14]. The n.m.r. triad tacticity was determined from methyl carbon resonance data. The ethylene content was also obtained using i.r. spectroscopy using a Nicolet 510 FTIR spectrometer coupled to a Nicolet 620 data station. The samples were compression moulded between hot plates at 483 K into 0.2 mm thick films. The i.r. spectra, including 128 scans at 2 $\mathrm{cm^{-1}}$ resolution, were recorded at room temperature. The total ethylene content was determined using the area of the absorption peak at 733 $\mathrm{cm^{-1}}$. The height of the peak was used to determine the amount of statistically distributed ethylene units[15,16]. The absorption at 809 $\mathrm{cm^{-1}}$ was used as internal standard. Standards of poly(propylene-*stat*-ethylene) copolymers with known ethylene content in the composition range 1.5–9.4 mol% ethylene were used for calibration.

Data for molar mass, ethylene content and tacticity of studied fractions are presented in *Tables 1* and *2*. Some differences were observed between the data for the ethylene content obtained by n.m.r. and i.r. spectroscopy.

Most thermal treatment of samples studied by the different techniques was carried out in a Perkin-Elmer DSC-7 apparatus.

Differential scanning calorimetry

Heat of fusion data were obtained in a temperature- and energy-calibrated Perkin-Elmer DSC-7 d.s.c. using N_2 as purge gas. Samples weighing 6 ± 1 mg enclosed in Al-pans were melted and kept at 458 K for 6 min before being cooled at a rate of 80 K $\mathrm{min^{-1}}$ to the chosen crystallization temperature (T_c). After crystallization, the samples were cooled at 320 K $\mathrm{min^{-1}}$ to room temperature. Some samples were cooled from the melt

Table 1 Molecular structure of studied fractions

C_2 content (mol%)			Randomness (%)[b]			
N.m.r.	I.r.	Fraction type[a]	N.m.r.	I.r.	$\bar{M}_n$ (g $\mathrm{mol^{-1}}$)	M_w (g $\mathrm{mol^{-1}}$)
0.0		m		–	35 000	50 000
2.7	3.6	m	98	79	169 000	453 000
5.7	5.4	m	74	75	217 000	474 000
6.9	8.5	e	78	68	34 000	151 000
8.7	6.6	e	58	70	63 000	254 000
11.0	9.3	e	64	63	34 000	152 000

[a] The designations e and m refer to fractionation according to ethylene content and to molar mass, respectively
[b] Randomness, percentage of structures having one ethylene unit between propylene units

Table 2 N.m.r. data of fractions studied

	C_2 distribution			Propylene tacticity[d]		
C_2 content (mol%)	Random[a] (%)	Block[b] (%)	Effective C_2 content (mol%)[c]	Isotactic (%)	Syndiotactic (%)	Atactic (%)
0	0	0	0	94.4	2.7	2.9
2.7	98	0	2.7	96.3	1.4	2.3
5.7	74	5	4.9	95.5	1.7	2.8
6.9	78	5	6.1	92.5	3.7	3.8
8.7	58	10	6.8	93.1	2.2	4.7
11.0	64	10	9.0	89.9	3.9	6.2

[a] One ethylene unit between propylene units
[b] Four or more ethylene units between propylene units
[c] 100 × (number of ethylene sequences): (number of ethylene sequences + number of propylene units)
[d] Based on triads

to room temperature at a rate of 10 or 80 K min^{-1}. Data for the heat of fusion obtained at a heating rate of 10 K min^{-1} were transformed into mass crystallinities (w_c) using total enthalpy method[17]:

$$w_c = \frac{\Delta h_f}{\Delta h_f^0 - \int_{T_1}^{T_m^0} (c_{pa} - c_{pc}) dT} \tag{1}$$

where T_1 is an arbitrary temperature below the melting range, and c_{pc} and c_{pa} are the specific heats of the crystalline and amorphous components, respectively. 209 kJ kg^{-1} was used as the heat of fusion (Δh_f^0) and 460.7 K as the equilibrium melting point, T_m^0[15]. Specific heat data given by Wunderlich[18] were used.

Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) patterns were obtained using a focusing Guinier–Hägg camera with subtraction geometry on isothermally crystallized samples cooled to room temperature. Finely powdered silicon was added as internal 2θ-standard. Strictly monochromatized CuKα_1 radiation with $\lambda = 0.1540598$ nm[19] and single-coated films were used. The scattered intensity of the films was measured by a computer-controlled single-beam microdensitometer. Step-intensity data calculated by the computer program SCANPI were used as input data to a Rietveld refinement program, DBW 3.2S[20]. Positional coordinates for the atoms were fixed to the values given for the α crystal form of polypropylene by Natta and Corradini[21]. The 2θ range used for the refinements was $9° < 2\theta < 19.5°$ and $20.5° < 2\theta < 60°$. The gap in the 2θ-range was due to reflection from γ crystals. Only non-structural parameters and cell dimensions were refined. This procedure was used in order to overcome the problem with overlapping diffraction peaks of the α and γ crystal forms. The γ crystal content of the samples was obtained according to Turner-Jones[4].

The mass crystallinity was assessed in a Stoe Stadi/P powder diffractometer operating in the symmetric transmission mode, with a rotating polymer sample. The X-ray beam used was strictly monochromatized CuKα_1 radiation ($\lambda = 0.1540598$ nm)[19] and the data were collected with a small linear position-sensitive detector covering 6.4° in 2θ. The data collection method was checked using a detector opening of only 2° in 2θ. No significant difference was found between data collected with the two detector openings. In order to reduce the influence of variations in absorption and also because $I_{cr}(s)$ is usually negligible above $2\theta = 55°$, the measurements were restricted to $7° < 2\theta < 63°$.

An interactive program was written to determine the degree of crystallinity founded on principles described by Ruland[22], based on:

$$w_c = \left[\int_{s_0}^{s_p} s^2 \cdot I_c(s) \cdot ds \Big/ \int_{s_0}^{s_p} s^2 \cdot I(s) \cdot ds\right] \cdot K\left(s_0, s_p, D, f^{-2}\right) \tag{2}$$

where w_c is the mass crystallinity, $s = (2/\lambda)\sin(\theta)$, θ = diffraction angle, λ = wavelength, $I_c(s)$ is the part of the coherent scattering concentrated into the diffraction peaks, and $I(s)$ is the total coherent scattering measured in electron units, normalized with respect to the average scattering per atom. D is the isotropic 'disorder' function that takes into account the loss of intensity at the reciprocal-lattice points due to deviations of the atoms from their ideal positions, and $\bar{f}^2 = \Sigma N_i f_i^2 / \Sigma N_i$, where f_i is the scattering factor of an atom of type i, N_i is the number of atoms of type i, and K are the values taken from the nomogram calculated for polypropylene by Ruland[22].

The designation 'crystalline' is restricted to crystalline regions larger than 2–3 nm, and containing no lattice imperfections of the second kind greater than an r.m.s. deviation of about 10% in the nearest neighbour distances.

Ruland[22] showed that it is possible to choose a number of integration intervals (limits s_0 and s_p) and to solve equation (2) by determining the series of K-values for a given disorder function $D = \exp(-ks^2)$ which yield crystallinity values which are approximately constant for all integration intervals. The factor k includes the effects of thermal motion and of lattice imperfections in general. The main difficulty in applying this method is that the intensities have to be scaled to electron units, normalized to the average scattering per atom, and corrected for the incoherent Compton scattering. In order to overcome these difficulties, the original intensity scale for $I_c(s)$ and $I(s)$ is used and the computer is allowed to rescale the incoherent scattering function to the level where the integration interval gives the most constant degree of crystallinity. The shape of the incoherent scattering curve is described by the analytical function given by Smith Jr. *et al.*[23]:

$$I_{inc}(s) = Z \cdot \left[1 - \left(1 + a \cdot s^2 + b \cdot s^4\right) \cdot \left(1 + c \cdot s^2 + d \cdot s^4\right)^{-2}\right] \tag{3}$$

The parameters a, b, c and d have been tabulated by Smith Jr. *et al.*[23] and values for carbon are used. The factor Z, originally defined as the atomic number for a neutral atom, is now treated as a general scale factor to be determined in order to put $I_{inc}(s)$ on the same scale as $I_c(s)$ and $I(s)$.

When using the computer program, the observed X-ray intensities are automatically corrected for polarization, and a graphic output of $s^2 \cdot I(s)$ *versus* s is displayed. The amorphous halo is defined by drawing a curve from the bases of the crystalline Bragg peaks. The program is designed to calculate the w_c-values for the selected integration intervals s_0 to s_p by varying the k-parameter and the scale factor Z in a step-wise manner.

The crystallinity values for the different integration intervals are tabulated and a formal 'standard deviation' is calculated to find the group of crystallinity values showing the least variations. An average of these values is taken as a degree of crystallinity. Using a limited 2θ-range, the crystallinity values are not greatly affected by errors in the scale factor Z. The background of each run is saved and can be displayed in a new run, when small variations in the background curve are tested. The definition of the background is extremely important for the result. Several runs were therefore performed to obtain the optimum curve.

Infra-red spectroscopy

The helical order at room temperature of samples given a specified thermal treatment in the d.s.c.

Table 3 Degree of crystallinity and heat of fusion data

C_2 content (mol%)	T_c[a] (K)	ΔH_m[b] ($J g^{-1}$)	Mass crystallinity D.s.c.[c] (%)	 WAXS (%)	γ content (%)[d]	ΔH_m / w_c (WAXS)
0	373	97 ± 2	49	49 ± 1	0	198 ± 8
2.7	373	75 ± 2	40	36 ± 1	18	208 ± 12
5.7	373	70 ± 2	39	38 ± 1	28	184 ± 10
5.7	393	70 ± 2	38	34 ± 1	72	206 ± 16
5.7	403	71 ± 2	39	36 ± 1	53	197 ± 12
8.7[e]	$80 K min^{-1}$	62 ± 2	36	30 ± 1	12	206 ± 15
8.7	373	59 ± 2	32	33 ± 1	35	179 ± 12
8.7	388	59 ± 2	32	36 ± 1	70	164 ± 10
8.7	393		-	37 ± 1	75	-
11.0	373	59 ± 2	33	37 ± 1	49	159 ± 10
11.0	393	62 ± 2	36	35 ± 1	79	177 ± 11

[a] Crystallization temperature
[b] Melting enthalpy
[c] Calculated using values for alpha form only
[d] γ content in the crystalline component
[e] Sample cooled from the melt directly to room temperature at $80 K min^{-1}$

apparatus was studied by i.r. spectroscopy (Perkin-Elmer FTIR 1760X spectrometer using 25 scans with a resolution of $2 cm^{-1}$). A few samples were melted in a hot stage (temperature control: ±1 K) and the i.r. spectrum was recorded for the molten polymer.

Small-angle X-ray scattering

Long period data were obtained by small-angle X-ray scattering (SAXS). A pinhole-collimated Rigaku camera attached to a Cu rotating anode source operating at 140 mA and 40 kV was used to obtain the small angle X-ray scattering patterns. The sample-to-film distance was 330 mm and the exposure time was 30 h. The scattered intensities were obtained from the films using a microdensitometer. The scattered intensity was obtained as a function of scattering angle (θ) by averaging a number of diametrical readings through the centre of the main beam position and subtracting the background from the intensity curve. The reduced scattered intensity curve ($I = f(\theta)$) was divided into a Gaussian background and a Bragg peak which was fitted into one or several Lorentzian components using a least-squares-fitting procedure according to:

$$I = I_0 e^{-\left(\frac{2(\theta-\theta_0)}{\alpha_0}\right)^2} + \frac{I_1}{\left(1+\left(\frac{2}{\alpha_1}(\theta-\theta_1)\right)^2\right)^2} \qquad (4)$$

where I_0 and I_1 are scattered intensities associated with the Gaussian and the Lorentzian functions respectively, and θ_0, θ_1, α_0 and α_1 are adjustable variables. The Lorentz correction[24] was applied: the s-values (s_{max}) associated with the maximum in $I(\text{Lorentz}) \cdot s^2 = f(s)$ [$s = 2\sin\theta/\lambda$, λ = wavelength] was determined and the long period (L) was obtained according to:

$$L = \frac{1}{s_{max}} \qquad (5)$$

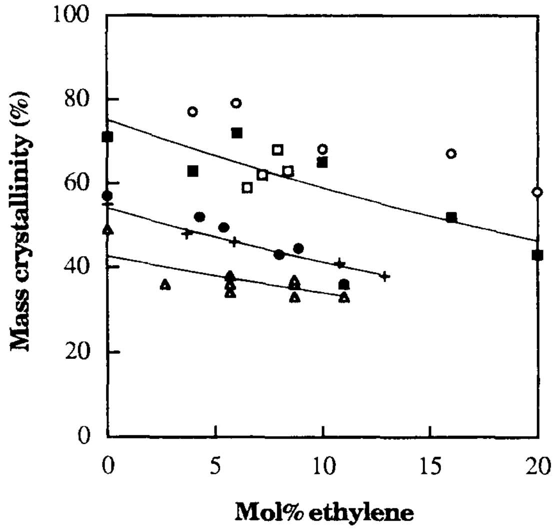

Figure 1 Crystallinity obtained by WAXS as a function of ethylene content. Previously published data by Zimmermann[1] (●), Avella *et al.*[2] (+), Guidetti *et al.*[5] (□), Busico *et al.*[3] (■ and ○ (annealed samples)) and data from present study (▲)

The average lamellar thickness (L_c) was calculated according to

$$L_c = v_c \cdot L \qquad (6)$$

where v_c is the volume crystallinity obtained by WAXS.

RESULTS AND DISCUSSION

Melting enthalpy and mass crystallinity data for isothermally crystallized samples are presented in *Table 3*. The agreement between the crystallinity data obtained by d.s.c. and by WAXS was good. The copolymer fractions exhibited significantly lower crystallinities than the homopolymer sample. The crystallinity was almost constant among the copolymer fractions.

Figure 1 presents a collection of earlier reported crystallinity data together with the data present in *Table 3* from the present work on statistical poly(propylene–ethylene) copolymers. An important feature of the data presented in *Figure 1* is that there is only a moderate decrease in mass crystallinity with increasing comonomer (ethylene) content, amounting to approximately 1% per mol% of ethylene comonomer. Wiberg *et al.*[7] showed that the decrease in mass crystallinity in poly(propylene-*co*-hexene-1) with increasing comonomer content was more than one order of magnitude greater than for the poly(propylene–ethylene) copolymers, 18% per mol% of hexene-1. Ethyl branches in polyethylene cause a reduction in crystallinity of approximately 20% per mol% of ethyl branch units[8].

It is also known that moderate changes in the tacticity of polypropylene have a profound effect on the resulting crystallinity. A 1% decrease in isotacticity in homopolymer fractions crystallized at high degrees of supercooling caused a 1% decrease in crystallinity[6,25]. Tacticity data for the polypropylene samples studied were not reported in the cited papers[1,2,4,5]. However, the tacticity data presented in *Table 2* show that the isotacticity is approximately constant in the studied samples, except for the sample with the highest ethylene concentration, in which isotacticity level is lower than in the other samples.

Another important feature of the data, presented in *Table 3*, is that there is a decrease in melting enthalpy for the poly(propylene-*stat*-ethylene) fractions of practically invariant X-ray crystallinity by $4\,\mathrm{J\,g^{-1}}$ per mol% ethylene. The magnitude of the decrease in melting enthalpy is in accordance with data for poly(propylene-*stat*-ethylene) reported by Avella *et al.*[2] and Zimmermann[1], whereas poly(propylene-*stat*-hexene) showed a much larger decrease in melting enthalpy, $35\,\mathrm{J\,g^{-1}}$ per mol% hexene-1[7]. The melting enthalpy data were normalized to values related to 100% crystallinity using the X-ray scattering data (*Table 3*). The data presented in *Table 3* for the poly(propylene-*stat*-ethylene)s indicate that there is a decrease in melting enthalpy for 100% crystalline polymer of $30–40\,\mathrm{J\,g^{-1}}$ per 10 mol% of ethylene comonomer. These differences could not be attributed to any variation in tacticity or γ crystal content. The recorded variation in melting enthalpy is considerably larger than expected from reported crystallinity data of polypropylene homopolymers of different isotacticities[6]. Zimmermann[1] reports invariant values for the normalized melting enthalpy of poly(propylene-*stat*-ethylene)s, in disagreement with the data of *Table 3*.

The observed moderate decrease in crystallinity with increasing ethylene content indicates that ethylene units are included in the crystalline component. Molecular mechanics modelling by Starkweather *et al.*[26] indicated that isolated single ethylene units and groups consisting of two ethylene units separated by two propylene units can be incorporated into the 3/1 helix with only a small increase in *intra*molecular free energy, $3.8\,\mathrm{kJ\,mol^{-1}}$. It was suggested[26] that an *inter*molecular interaction can partially compensate for this extra energy. Starkweather *et al.*[26] also reported that blocks of ethylene constitute a hindrance to the continuation of the 3/1 helix, whereas randomly occurring ethylene groups facilitate further helix propagation.

A comparison between the crystal thickness data and calculated data for the length distribution of ethylene-free segments in the copolymers provides information about the position of the ethylene units. A cumulative weight distribution ($W(n)$) for the ethylene-free propylene segments was obtained under the assumption that the ethylene groups have a statistical distribution along the chains according to the expression:

$$W(n) = \sum_{n=1}^{\infty} n(1-p)^2 p^{(n-1)} \tag{7}$$

where n is the number of propylene moieties in chain segments which are not interrupted by ethylene groups, and p is the molar content of propylene in the copolymer.

Figure 2 presents a graph (curve a) of the cumulative propylene-sequence-distribution in the copolymer with 11.0 mol% of ethylene units considering that a block content of 10% (*Table 2*) leads to a decrease in the 'effective' ethylene content to 9.0 mol%. The mass crystallinity of all copolymers is in the range 35–37% (*Table 3*) which, according to *Figure 3* (curve a), by selecting $W(n) = 1 - 0.35 = 0.65$, leads to an n-value of approximately 23. Crystallinity assessment by WAXS considers only crystals thicker than 2–3 nm[22], which corresponds to 9–13 repeating units. Thus, the considerable fraction of significantly longer ethylene-free chain segments indicates, according to this calculation, that the crystals are free of ethylene inclusions. However, if all the configurational defects were excluded from the crystals, the recorded crystallinity of 37% would not be reached (*Figure 2*, curve b). This curve is obtained by setting p equal to the propylene content minus the content of non-isotactic material using the data presented in *Table 2*. The relatively low crystallinity of the homopolymer, 49% according to the data presented in *Table 3*, means that only 56–60% of the isotactic (defect-free) segments crystallize. If the same proportion of the defect-free chain

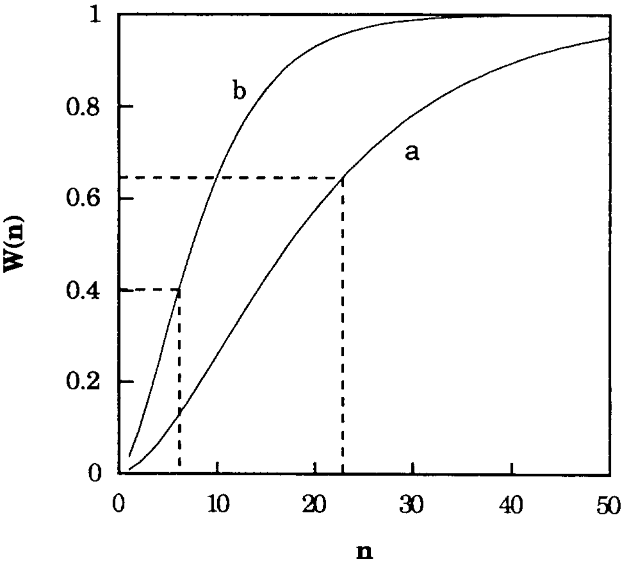

Figure 2 Cumulative distribution function (W_n) giving the mass fraction of propylene segments of different length calculated for a copolymer fraction with 11.0 mol% of ethylene, considering that the effective ethylene content is 9.0 mol% (curve a). Curve b considers also the stereoregularity and the distribution function of ethylene-free and isotactic polypropylene segments

segments, i.e. those free of ethylene groups and configurational defects, would crystallize in the copolymers, the limiting *n*-value becomes only 6 for the copolymer with 11.0 mol% of ethylene units, i.e. a value smaller than the required 9–13 repeating units detectable by WAXS. This comparison demonstrates that for this particular copolymer a portion of the ethylene groups are included in the crystals. The same conclusion may be drawn for the copolymer with 6.8 mol% of ethylene units, with a limiting *n*-value of 9, whereas the copolymers with lower ethylene contents showed limiting *n*-values greater than that of the threshold range for the WAXS analysis, i.e. greater than 9–13.

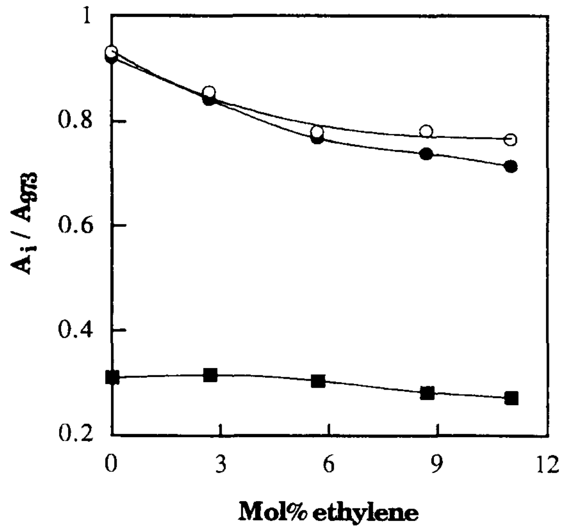

Figure 3 I.r. absorbance ratios A_{998}/A_{973} (○), A_{841}/A_{973} (●) and A_{900}/A_{973} (■) obtained at room temperature as a function of ethylene content

Table 4 Long period and lamellar thickness data

C_2 content (mol%)	T_c[a] (K)	L[b] (nm)	L_c[c] (nm)
0	373	10.5 ± 0.5	4.9 ± 0.3
5.7	373	12.7 ± 0.7	4.4 ± 0.3
8.7	373	12.1 ± 0.6	3.8 ± 0.3
8.7	388	14.3 ± 0.7	4.9 ± 0.4
11.0	373	14.0 ± 0.7	4.6 ± 0.4

[a] Crystallization temperature
[b] Long period
[c] Crystal thickness

It is assumed in the above analysis that the ethylene units are uniformly dispersed. The variations in ethylene content between different molecules in the e-fractions should be small, accordingly to Ogawa and coworkers[10–12], and the conclusions drawn from the above analysis should be correct.

The SAXS long period and crystal thickness remained essentially constant with changing ethylene content in the copolymer fractions (*Table 4*). The homopolymer showed a shorter long period but practically the same crystal thickness as the copolymers, which is consonant with the crystallinity data presented in *Table 3*.

The i.r. spectrum of polypropylene provides morphological information[27–31]. Most of the bands used for the assessment are not truly 'crystallinity bands' according to the strict definition of Zerbi *et al.*[32]. The bands associated with crystallinity are in fact due to the 3/1 helices. The absorption bands at 998 cm^{-1} and 841 cm^{-1} are associated with helices with respectively at least 11–12 and 13–15 repeating units[29]. The peak at 900 cm^{-1} is related to the crystalline phase[28]. The absorption peak at 973 cm^{-1} is suggested to be of mixed character[28,30] or to arise from at least five repeating units with helical order[29]. I.r. of a high molar mass copolymer sample with 5.7 mol% of ethylene units were obtained at different temperatures. Both the 998 cm^{-1} and 841 cm^{-1} bands disappeared completely when the sample was molten, whereas the 900 cm^{-1} band also showed a small intensity of the molten state of the polymer at 463 K. The 973 cm^{-1} and 2725 cm^{-1} bands lost respectively 20% and 40% of their room temperature intensities on melting. The 973 cm^{-1} band was thus selected as an internal standard with which the aforementioned absorption bands were compared for samples crystallized at 373 K (*Figure 3*). All the spectra were taken at room temperature.

Table 5 Unit cell parameters at room temperature

Ethylene-content (mol%)	T_c[a] (K)	a (nm)	b (nm)	c (nm)	β (°)	Cell volume ($(nm)^3$)
Nattas cell[21]	–	0.665	2.096	0.650	99.2	0.894
0	388	0.664 ± 0.001	2.096 ± 0.002	0.651 ± 0.002	98.7 ± 0.2	0.896 ± 0.005
2.7	373	0.670 ± 0.001	2.119 ± 0.002	0.657 ± 0.002	98.6 ± 0.2	0.922 ± 0.006
4.1[b]	373	0.668 ± 0.001	2.113 ± 0.002	0.654 ± 0.002	98.8 ± 0.4	0.912 ± 0.006
5.7	373	0.667 ± 0.001	2.115 ± 0.002	0.655 ± 0.003	98.5 ± 0.3	0.914 ± 0.007
6.9	373	0.665 ± 0.002	2.108 ± 0.004	0.656 ± 0.005	98.8 ± 0.4	9.909 ± 0.012
8.7	373	0.667 ± 0.001	2.114 ± 0.002	0.656 ± 0.002	98.5 ± 0.2	0.915 ± 0.005
8.7[c]	10 K min^{-1}	0.668 ± 0.001	2.111 ± 0.002	0.654 ± 0.003	98.6 ± 0.4	0.912 ± 0.007
8.7[c]	80 K min^{-1}	0.668 ± 0.001	2.112 ± 0.002	0.656 ± 0.003	98.5 ± 0.3	0.915 ± 0.007
8.7[c]	200 K min^{-1}	0.668 ± 0.001	2.107 ± 0.002	0.656 ± 0.002	98.9 ± 0.2	0.912 ± 0.006
11.0	373	0.666 ± 0.001	2.114 ± 0.003	0.656 ± 0.003	98.5 ± 0.2	0.913 ± 0.007

[a] Crystallization temperature
[b] Ethylene content measured by i.r.
[c] Sample is cooled from melt directly to room temperature at quoted cooling rates

Both A_{841}/A_{973} and A_{998}/A_{973} decreased monotonously with increasing ethylene content, with a slightly stronger effect for A_{841}/A_{973} (*Figure 3*). The other selected absorption band ratio (A_{900}/A_{973}) decreased only moderately with increasing ethylene content. The results indicate a 10–15% decrease in the content of 3/1 helices of minimum lengths 11–12 or 13–15 repeating units in the copolymer samples with increasing ethylene content (2.7–11.0 mol%). These samples showed, however, practically the same X-ray crystallinity (*Table 3*). These apparently contradicating sets of data may be explained by the presence of ethylene units in the crystals which cause an interruption in the 3/1 helix. Such 'terminations' of the 3/1 helices are accounted for in the results obtained by i.r. spectroscopy. However, the ethylene units cause, according to Starkweather *et al.*[26], only a moderate disturbance of the crystal structure. The results may thus be explained as being due to a gradual increase in concentration of short 3/1 helices consisting of less than 11–12 (13–15) repeating units in the crystalline phase with increasing ethylene content.

Data for the unit cell parameters of the α crystal form are presented in *Table 5*. The homopolymer showed cell parameters the same as those of the cell originally reported by Natta and Corradini[21]. The unit cell of the copolymers expanded mainly along b. The results are noticeably different from earlier reported data, the latter either being constant[1,3] or showing a decreasing trend[2] with increasing ethylene content. It should also be noted that the crystal thickness was practically constant in all the samples studied (*Table* 4). The cell expansion due to the observed variation in tacticity (*Table 2*) should be very small as judged by the data of Cheng *et al.*[6], who observed an expansion in the α unit cell volume from 0.930 $(nm)^3$ to 0.938 $(nm)^3$ with a change in isotacticity from 98.8% to 78.7%. The cell parameters for all the copolymer fractions were the same and independent of ethylene content. This striking result may be taken as evidence in favour of an expansion of the unit cell due to ethylene-unit inclusion in the crystals. The reason for the lack of linearity of the cell expansion with overall ethylene content can only be speculated on. It may indicate that the degree of ethylene-inclusion in the α crystals is constant in the copolymer samples. Another possible explanation may be that the cell expansion is greater as a result of isolated ethylene-inclusions than with groups of crystalline ethylene units.

CONCLUSIONS

With increasing ethylene content (2.7–11.0 mol%), poly(propylene-*stat*-ethylene) melt-crystallized at 373 K showed only a moderate decrease in X-ray crystallinity, a small decrease in melting enthalpy, a constant crystal thickness and a shortening in average length of 3/1 helices, which indicates that a fraction of the ethylene units are included in the crystals.

ACKNOWLEDGEMENTS

This study was sponsored by the Neste Foundation, Finland and CICYT, Spain (grant MAT 94-0825). H. Crozier is thanked for the fractionation work of the copolymer fractions, T. Väänänen for the n.m.r. spectroscopy and G. Wiberg for the preparation of the homopolymer fraction.

REFERENCES

1 Zimmermann, H. J. *J. Macromol. Sci.-Phys.* 1993, **B32**, 141
2 Avella, M., Martucelli, E., Della Volpe, G., Segre, A., Rossi, E. and Simonazzi, T. *Makromol. Chem.* 1986, **187**, 1927
3 Busico, V., Corradini, P., De Rosa, C. and Di Benedetto, E. *Eur. Polym. J.* 1985, **21**, 239
4 Turner-Jones, A. *Polymer* 1971, **12**, 487
5 Guidetti, G. P., Busi, P. and Giulianelli, I. *Eur. Polym. J.* 1983, **19**, 757
6 Cheng, S. Z. D., Janimak, J. J., Zhang, A. and Hsieh, E. T. *Polymer* 1991, **32**, 648
7 Wiberg, G., Werner, P.-E. and Gedde, U. W. *Mater. Sci. Eng.* 1993, **A173**, 173
8 Wunderlich, B. 'Macromolecular Physics', Vol. 3. Academic Press, New York, 1980
9 Turner-Jones, A. *Polymer* 1966, **7**, 23
10 Owaga, T., Tanaka, S. and Inaba, T. *J. Appl. Polym. Sci.* 1973, **17**, 319
11 Owaga, T. and Inaba, T. *J.Polym. Sci., Polym. Phys. Edn* 1974, **12**, 785
12 Owaga, T., Tanaka, S. and Inaba, T. *J. Appl. Polym. Sci.* 1974, **18**, 3345
13 Lehtinen, A. and Paukkeri, R. *Macromol. Chem. Phys.* 1994, **195**, 1539
14 Randall, J. C. *J. Macromol. Chem. Phys.* 1989, **C29**, 201
15 Topi, C. and Ciampelli, F. *Adv. Polym. Sci.* 1973, **11**, 88
16 Baker, Jr., B. B., Bobesteel, J. K. and Keating, M. Y. *Thermochim. Acta* 1990, **166**, 53
17 Gray, A. P. *Thermochim. Acta* 1970, **1**, 563
18 Wunderlich B., 'ATHAS—Table of Thermal Properties', University of Tennessee, Knoxville, USA, 1993
19 Deslattes, R. D. and Henins, A. *Phys. Rev. Lett.* 1973, **31**, 2864
20 Wiles, D. B., Sakthivel, A. and Young, R. A. 'Users Guide to Program DBW 3.2S for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns (Version 8804)', School of Physics, Georgia School of Technology, Atlanta, USA
21 Natta, G. and Corradini, C. *Suppl. Nuovo Cimento* 1960, **15**, 40
22 Ruland, W. *Acta Crystallogr.* 1961, **14**, 1180
23 Smith, Jr., V. H., Thakkar, A. J. and Chapman, D. C. *Acta Crystallogr.* 1975, **A31**, 391
24 Christ, B. and Morosoff, N. *J. Polym. Sci., Polym. Phys. Edn* 1973, **11**, 1023
25 Paukkeri, R. and Lehtinen, A. *Polymer* 1993, **34**, 4075
26 Starkweather, Jr., H. W., Van-Catledge, F. A. and MacDonald, R. N. *Macromolecules* 1982, **15**, 1600
27 Samuels, R. J. *Makromol. Chem. Suppl.* 1981, **4**, 241
28 Houska, M. and Brummel, M. *Polym. Eng. Sci.* 1987, **27**, 919
29 Kissin, Y. V. and Rishina, L. A. *Eur. Polym. J.* 1976, **12**, 757
30 Burfield, D. R. and Loi, P. S. T. *J. Appl. Polym. Sci.* 1989, **36**, 279
31 Passingham, C., Hendra, P. J., Cudby, M. E. A., Zichy, V. and Weller, M. *Eur. Polym. J.* 1990, **26**, 631
32 Zerbi, G., Ciampelli, F. and Zamboni, V. *J. Polym. Sci., Polym. Symp.* 1964, **7**, 141