

# Crystallization kinetics and morphology of 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

Department of Structural Chemistry, University of Stockholm, S-106 91 Stockholm, Sweden

and J. Martinez-Salazar

Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain

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The crystallization and melting behaviour and the morphology of fractions of poly(propylene-*stat*-ethylene) with 2.7–11.0 mol% ethylene were studied by differential scanning calorimetry, wide-angle X-ray scattering, polarized light microscopy and transmission electron microscopy, after etching with permanganic acid. The inclusion of ethylene co-repeating units in isotactic polypropylene (0–11.0 mol% ethylene) caused approximately linear decreases in kinetic and equilibrium melting temperatures and in the glass transition temperature with increasing ethylene content. X-ray scattering showed that the content of the  $\gamma$  form increased with increasing ethylene content, increasing crystallization temperature and decreasing cooling rate from the molten state. It was shown for one of the copolymers (8.7 mol% ethylene) that during heating approximately 50% of the  $\gamma$  form was converted to the  $\alpha$  form before the final melting of the sample. The rest of the  $\gamma$  crystals melted without transformation to the  $\alpha$  form. The multimodality of the crystal melting above the crystallization temperature in the polymers with a more uniform crystal structure was caused by recrystallization during heating, whereas polymers with appreciable contents of both  $\alpha$  and  $\gamma$  forms exhibited multimodal melting at all the heating rates adopted. The size of the low temperature melting peak as assessed at a heating rate of 40 K min<sup>-1</sup> was approximately proportional to the initial content of the  $\gamma$  form. By comparison with the spherulitic structure of homopolymers, that of the copolymers was coarser with internal and peripheral pockets of molten material during spherulite growth. The crystal lamellae exhibited more curvature in the copolymer samples than in the homopolymer. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

Statistical copolymers based on propylene as the major component and ethylene, hereinafter denoted poly(propylene-*stat*-ethylene), crystallize from the molten state into the so-called  $\alpha$  and  $\gamma$  forms<sup>1</sup>. The content of the  $\gamma$  form increases with increasing ethylene content<sup>1–3</sup>. Turner-Jones<sup>1</sup> suggested earlier that the development of the  $\gamma$  form is due to interruptions in the isotactic sequences, which in a copolymer is accomplished by the comonomer units. The development of the  $\gamma$  form is favoured by a slow cooling from the melt, particularly in cases where crystal nuclei are present in the melt prior to cooling<sup>1</sup>. In a copolymer sample with a mixture of  $\alpha$  and  $\gamma$  crystals, the  $\gamma$  crystals either melt at relatively low temperatures or are converted to the  $\alpha$  form and leave almost pure  $\alpha$  crystals to melt at higher temperatures<sup>1,2</sup>. A synchrotron X-ray diffraction study<sup>4</sup> of a slowly cooled melt of poly(propylene-*stat*-ethylene) with 4 mol% ethylene units showed that  $\alpha$  crystals were initially

formed at 383 K and that  $\gamma$  crystals developed at lower temperatures, typically at temperatures below 373 K.

In a parallel paper<sup>5</sup>, data from X-ray scattering are reported that led us to the conclusion that a significant portion of the ethylene units are included in the crystals. This conclusion is principally in accordance with earlier reports of Avella *et al.*<sup>6</sup> and Busico *et al.*<sup>7</sup> but in disagreement with the conclusions drawn by Zimmerman<sup>8</sup>.

Monasse and Haudin<sup>9</sup> observed in a copolymer with 4.1 mol% of ethylene units that there was a change in growth rate kinetics and supermolecular structure at temperatures between 399 and 403 K: negative spherulites were formed at temperatures above 403 K whereas crystallization at temperatures below 399 K resulted in positive spherulites. The growth rate kinetics changed at the transition temperature from regime II to regime III according to the theoretical scheme introduced by Clark and Hoffman<sup>10</sup>. The initial morphology as assessed by polarized microscopy as either 'quasi-circular' or 'elongated'<sup>9</sup>. Both features are essentially different views of the same structure, the quadrite, which is the

\* To whom correspondence should be addressed

cross-hatched morphology consisting of planar arrays of quasi-orthogonal intercrossing  $\alpha$  crystals<sup>11</sup>.

The relatively few reports published on morphological aspects of poly(propylene-*stat*-ethylene)s are concerned with unfractionated samples with a non-uniform chain structure. This paper presents data for fractions in which large internal variations in comonomer content, configurational defect concentrations and molar mass have been eliminated. Data for copolymers with 0 to 11.7 mol% ethylene units with regard to polymorphism, melting behaviour, lamellar and spherulitic structure and kinetics of crystallization are reported.

## EXPERIMENTAL

Preparation and characterization of the poly(propylene-*co*-ethylene) fractions used in this study are described in a previous paper<sup>5</sup> and a summary of the data is presented in Table 1.

Crystallization kinetics data were obtained in a differential scanning calorimeter (d.s.c., Perkin-Elmer DSC-7) on  $6.0 \pm 1.0$  mg samples and in a Leitz Ortholux POL BK II polarized microscope equipped with Mettler Hot Stage FP 82 on  $5 \mu\text{m}$  thick films after 6 min storage at 458 K to ensure complete melting,  $80 \text{ K min}^{-1}$  ( $20 \text{ K min}^{-1}$  for polarized microscopy) cooling to the crystallization temperature after which crystallization was recorded calorimetrically (exothermal enthalpy was converted to mass crystallinity using  $207 \text{ J g}^{-1}$  as the heat of fusion of 100% crystalline polymer<sup>12</sup>) or by measurement of the spherulite radius growth rate based on 5–8 growing spherulites under the isothermal conditions. After the crystallization was complete under the isothermal conditions, the samples were either heated at a rate of  $10 \text{ K min}^{-1}$  in the d.s.c. apparatus while recording the melting trace, or cooled at  $320 \text{ K min}^{-1}$  to room temperature, after which the melting trace was obtained during the subsequent  $10 \text{ K min}^{-1}$  heating scan. Both crystallization and melting traces were obtained during  $10 \text{ K min}^{-1}$  cooling and heating scans between 213 K and 458 K.

Recorded melting enthalpies were transformed into mass crystallinities ( $w_c$ ) as described in the parallel paper<sup>5</sup>. The overall mass crystallinity and the  $\gamma$  crystal content were also obtained by wide-angle X-ray scattering

(WAXS) using a Stoe Stadi/P powder diffractometer as described in the previous paper<sup>5</sup>. The  $\gamma$  form content was assessed according to the method of Turner-Jones<sup>1</sup>. The content of the different crystal phases during transitional stages during crystallization and melting were obtained from the diffraction patterns recorded in a diffractometer equipped with a Rigaku Denki vertical goniometer operating in the reflection mode using  $\text{CuK}\alpha_1$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). An Anton Paark TTK2-HC Heat Controller was used to control the temperature and the intensity of the scattered X-rays was determined in a scintillation detector with pulse height discrimination.

The samples for transmission electron microscopy (TEM) were first crystallized under isothermal conditions in the d.s.c. apparatus, freeze-polished at 193 K and treated with a solution of  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  according to the method described by Sneek<sup>13</sup> which is essentially based on the methodology of Olley and Bassett<sup>14</sup>. Some of the samples were crystallized in contact with Mylar<sup>®</sup> [biaxially stretched poly(ethylene terephthalate)]. The etched samples were shadowed with Au/Pd (80/20) and coated with carbon, and direct replicas using poly(acrylic acid) were taken. The replicas were examined in a JEOL JEM 100 B electron microscope.

## RESULTS AND DISCUSSION

Figure 1 shows that both crystallization and melting temperatures recorded during cooling and heating scans at  $10 \text{ K min}^{-1}$  decreased by approximately  $3 \pm 0.3 \text{ K}$  per mol% of ethylene units. The width of the melting temperature range was approximately the same, approximately 60 K, for all the fractions whereas unfractionated copolymer samples melted over a temperature range of 80 K. The broader melting range in the unfractionated samples was due to the presence of low molar mass and defect-rich species. These species were removed by the fractionation. The glass transition temperature ( $T_g$ ) decreased by  $1.6 \text{ K}$  per mol% of ethylene units (Figure 1). These data are in accordance with previously published data for unfractionated ethylene-copolymers<sup>15</sup>.

The poly(propylene-*stat*-ethylene) fractions crystallized under isothermal conditions in the temperature range 373–403 K and, when heated directly after the

**Table 1** Molecular structure of studied fractions

$\text{C}_2$ content (mol%) <sup>a</sup>	Random $\text{C}_2$ / Block $\text{C}_2$ <sup>b</sup> (%)	$\bar{M}_n$ <sup>c</sup> ( $\text{g mol}^{-1}$ )	$\bar{M}_w$ <sup>c</sup> ( $\text{g mol}^{-1}$ )	Fraction type <sup>d</sup>	Isotacticity <sup>b</sup>
0	0/0	35 000	50 000	m	94.4
2.7	98/0	169 000	453 000	m	96.3
4.1*	—/—	74 000	116 000	m	
5.7	74/5	217 000	474 000	m	95.5
5.9	89/2	79 000	280 000	e	
6.5*	—/—	71 000	105 000	m	
6.6*	—/—	45 000	154 000	e	
6.9	78/5	34 000	151 000	e	92.5
8.7	58/10	63 000	245 000	e	93.1
11.0	64/10	34 000	152 000	e	89.9

<sup>a</sup> By  $^{13}\text{C}$  n.m.r. or i.r. spectroscopy (marked with asterisk)

<sup>b</sup> By  $^{13}\text{C}$  n.m.r. spectroscopy

<sup>c</sup> By size exclusion chromatography

<sup>d</sup> Fractionation according to ethylene content (e) or molar mass (m); for details see ref. 5

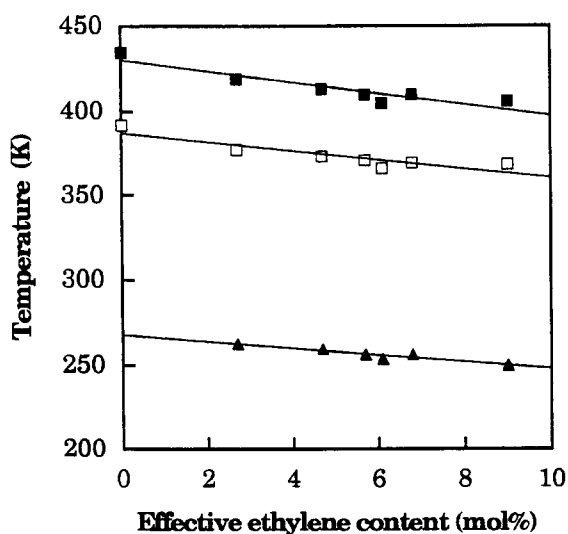


Figure 1 Melting (■) and crystallization (□) peak temperatures and glass transition temperature (▲) as a function of effective ethylene content in the copolymer (ref. 5). Data are based on thermograms recorded at  $10 \text{ K min}^{-1}$  scan rate

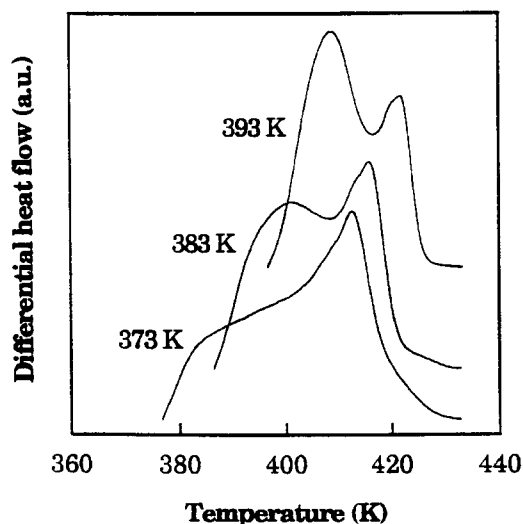


Figure 2 Melting thermograms of a copolymer sample (5.7 mol% ethylene) crystallized at different temperatures for more than  $8 \times$  the half time crystallization. The thermograms were recorded during direct heating at  $10 \text{ K min}^{-1}$  from the crystallization temperature

isothermal crystallization period, they exhibited bimodal melting (Figure 2). The relative size of the low temperature melting peak (shoulder) increased with increasing crystallization temperature ( $T_c$ ). The melting enthalpy and the width of the melting temperature range decreased with increasing crystallization temperature. The relative size of the low temperature peak increased and both peak temperatures decreased with increasing ethylene content (Figures 3 and 4). The relative size of the low temperature melting peak also increased with increasing crystallization temperature (Figures 3 and 4). WAXS data presented in Table 2 show that the content of the  $\gamma$  form at room temperature increased with increasing ethylene content, increasing crystallization temperature and decreasing cooling rate, principally in accordance with earlier reports<sup>1-3</sup>. The melting enthalpy including crystals of a melting point greater than 295 K showed no correlation with the  $\gamma$  form content but

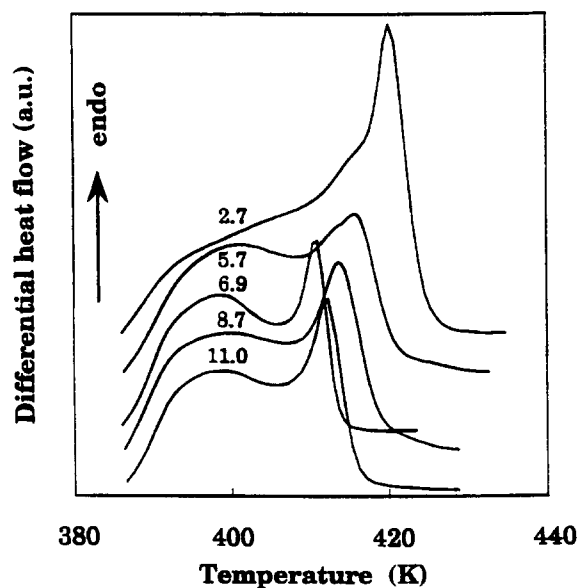


Figure 3 Melting thermograms of a series of copolymer samples with different ethylene contents (indicated in mol% adjacent to each curve) crystallized at 383 K for more than  $5 \times$  the half time crystallization. The thermograms were recorded during direct heating at  $10 \text{ K min}^{-1}$  from 383 K

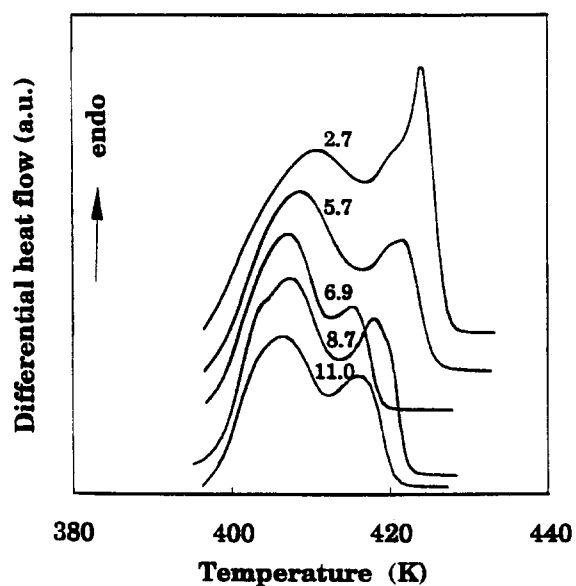
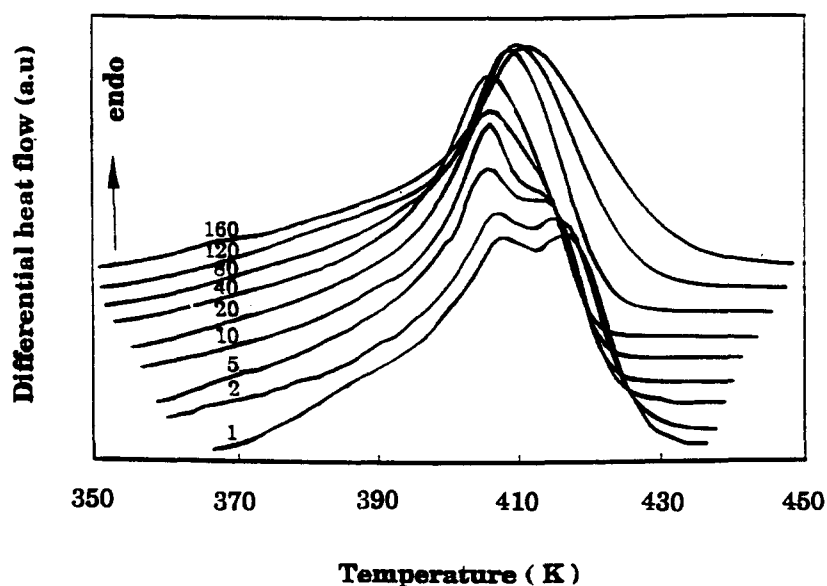


Figure 4 Melting thermograms of a series of copolymer samples with different ethylene contents (indicated in mol% adjacent to each curve) crystallized at 393 K for more than  $2 \times$  the half time crystallization. The thermograms were recorded during direct heating at  $10 \text{ K min}^{-1}$  from 393 K

exhibited a decreasing trend with increasing ethylene unit content which, according to a previous paper<sup>5</sup>, is due to inclusion of ethylene units in the crystals.

The equilibrium melting point  $T_m^0$ , as assessed by the Hoffman-Weeks method<sup>16</sup> using the high melting peak temperature data of samples crystallized to 5% crystallinity, showed, despite a considerable scatter in the data, an overall decrease by 2.3 K per mol% ethylene unit with increasing ethylene content which can be explained by partial inclusion of ethylene units in the crystals.

Figure 5 shows the effect of heating rate on the melting behaviour of a copolymer sample with 8.7% of ethylene



**Figure 5** Melting thermograms obtained at different heating for a copolymer sample (8.7 mol% ethylene) crystallized during a constant rate cooling ( $80 \text{ K min}^{-1}$ ) from the melt

**Table 2** Crystallinity data

$\text{C}_2$ content (mol%)	$T_c^a$ (K)	$\Delta H^b$ ( $\text{J g}^{-1}$ )	$w_c^c$ (%)	$\gamma$ content <sup>d</sup> (%)
0	373	97	49	0
2.7	373	75	36	18
4.1	373	80	—	21
5.7	373	70	37	28
6.5	373	—	—	44
6.9	373	65	—	60
8.7	373	59	33	35
11.0	373	59	35	49
5.7	383	73	—	—
6.9	378	62	—	68
6.9	383	64	—	81
6.9	388	66	—	84
8.7	388	59	36	70
5.7	393	70	33	72
8.7	393	—	—	72
11.0	393	62	35	79
5.7	403	71	36	53
8.7	$10 \text{ K min}^{-1}$	60	—	35
8.7	$80 \text{ K min}^{-1}$	62	30	12
8.7	$320 \text{ K min}^{-1}$	58	—	5

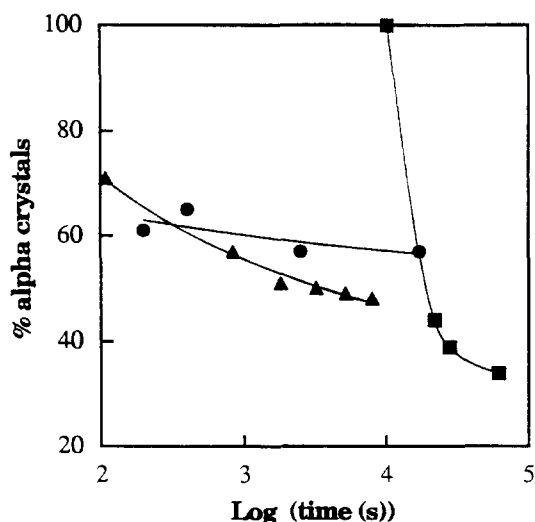
<sup>a</sup>Crystallization temperature; after the isothermal treatment the samples were cooled at  $320 \text{ K min}^{-1}$  to 296 K; the final three data are for samples crystallized during cooling at constant rate

<sup>b</sup>Melting enthalpy

<sup>c</sup>Mass crystallinity by WAXS at 296 K

<sup>d</sup>Fraction of  $\gamma$  form in crystalline component at 296 K

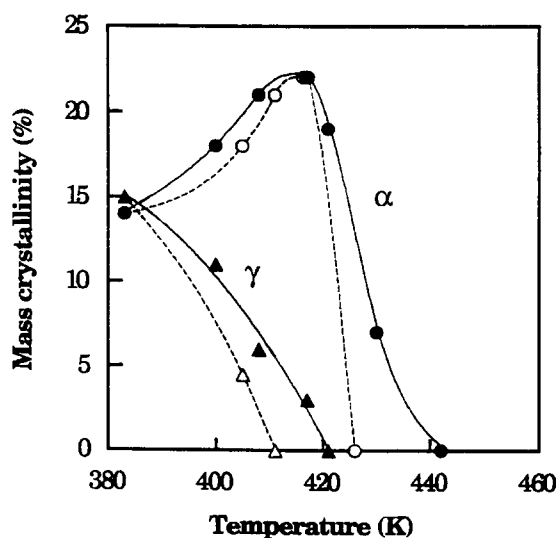
units originally crystallized during a  $80 \text{ K min}^{-1}$  cooling from the melt. The  $\gamma$  crystal content at room temperature of this sample was only 12%. Heating at 1 and  $2 \text{ K min}^{-1}$  led to a shift in the bimodal melting curve towards higher temperatures due to recrystallization and lamellar thickening. Melting was unimodal at the highest used heating rates ( $80$  and  $160 \text{ K min}^{-1}$ ) and the melting peak shifted towards higher temperatures with increasing heating rate, which indicates that superheating effects are dominant in this heating rate range. The bimodal nature of the melting curve was most apparent at low heating rates (Figure 5), indicative of recrystallization during heating. Paukkeri and Lehtinen<sup>17,18</sup> showed that the melting bimodality was present only in slowly heated samples of



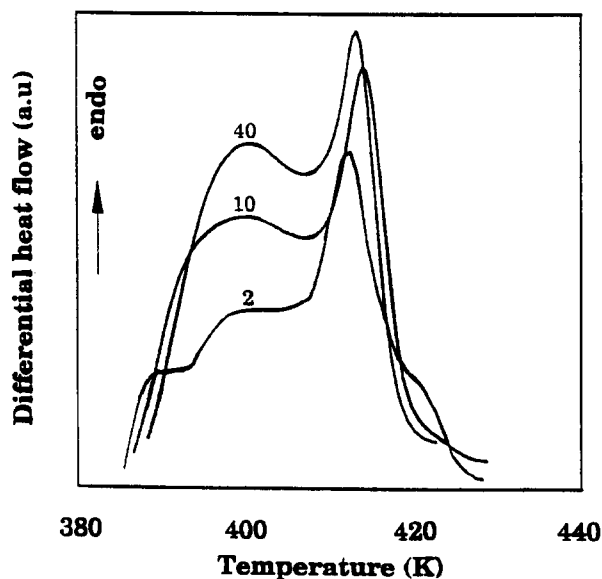
**Figure 6**  $\alpha$  Form content in the copolymer with 8.7 mol% ethylene units as a function of time during isothermal crystallization at 373 K (●), 383 K (▲) and 398 K (■)

a highly isotactic polypropylene fraction (homopolymer), whereas for a homopolymer fraction with lower isotacticity, melting was also bimodal at considerably higher heating rates, presumably due to the presence of a bimodal crystal thickness distribution in this particular sample. The high isotacticity (93%), the low initial  $\gamma$  crystal content (12%) and the small content of low molar mass species in the studied copolymer, together with the finding that ethylene units are partially included in the crystals<sup>5</sup>, are facts that together indicate that the high temperature melting peak appearing only during slow heating is due to recrystallization during heating.

WAXS showed that the initial crystallization at 383 K or higher was dominated by the  $\alpha$  crystal phase (Figure 6). The  $\gamma$  crystal content increased on prolonged crystallization, ultimately reaching values of 50% or greater at temperatures above 383 K (Figure 6). Figure 7 shows that approximately 50% of the  $\gamma$  form is converted to the more stable  $\alpha$  form during heating. The recrystallization



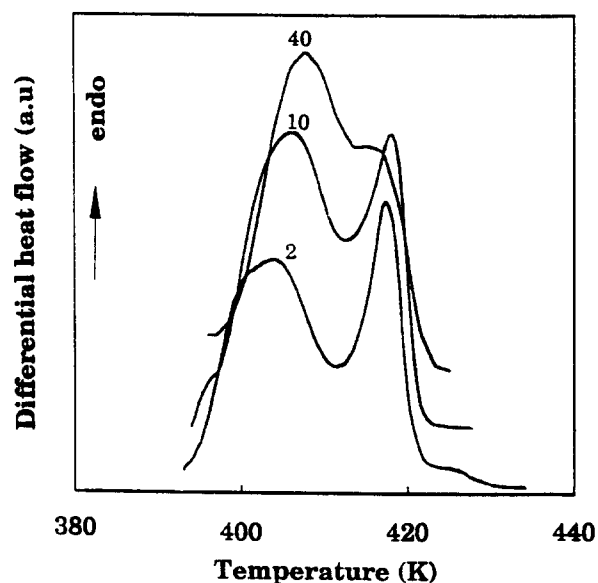
**Figure 7**  $\alpha$  Form (● and ○) and  $\gamma$  form (▲ and △) contents in the copolymer with 8.7 mol% ethylene units crystallized at 383 K for 90 min ( $20\times$  the half time crystallization) as a function temperature during stepwise heating ( $10\text{ K min}^{-1}$ ) from 383 K to 450 K. Filled symbols and continuous lines indicate data obtained during slower overall heating (longer isothermal periods: 30 min) and unfilled symbols and broken lines indicate data obtained during more rapid overall heating (shorter isothermal periods: 8 min)



**Figure 8** Melting thermograms of copolymer with 8.7 mol% ethylene units after crystallization at 383 K for 20 min ( $5\times$  the half time crystallization) recorded at three different heating rates as shown in the figure

started at temperatures between 390 and 400 K. The rest of the  $\gamma$  crystals melted directly without transformation to the  $\alpha$  crystal form. The heating rate dependence of the final melting point of the  $\gamma$  crystals evident in *Figure 7* constitutes evidence in favour of thickening of the  $\gamma$  crystals during heating. Polymorphic conversions from the  $\gamma$  to the  $\alpha$  form have been reported for homopolymers of isotactic polypropylene<sup>1</sup>.

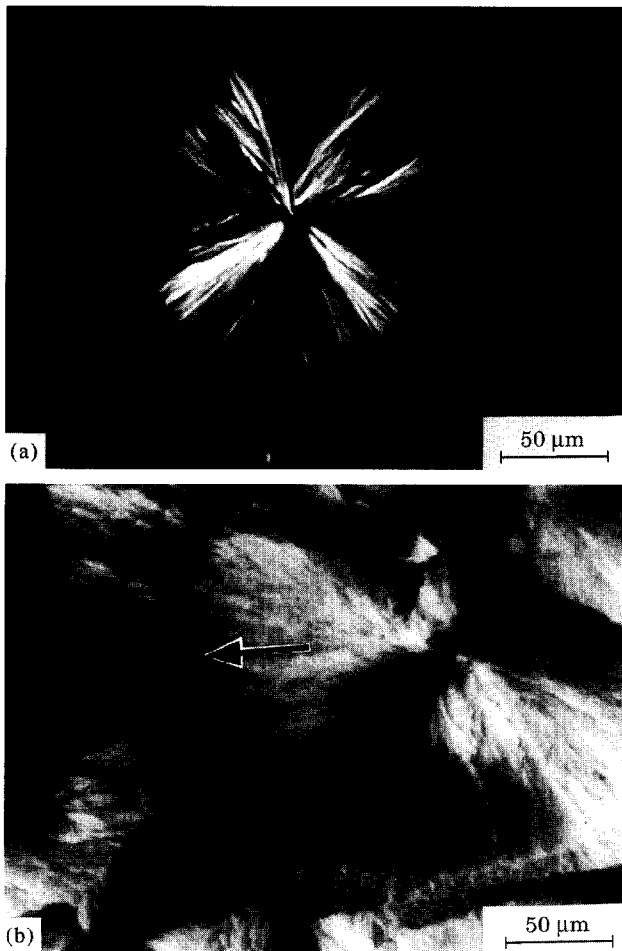
A qualitative relationship between the relative size of the low temperature peak (as recorded from direct heating after crystallization from the isothermal period) and the  $\gamma$  crystal content becomes evident when the data presented in *Figure 2* and *Table 2* are compared. The low



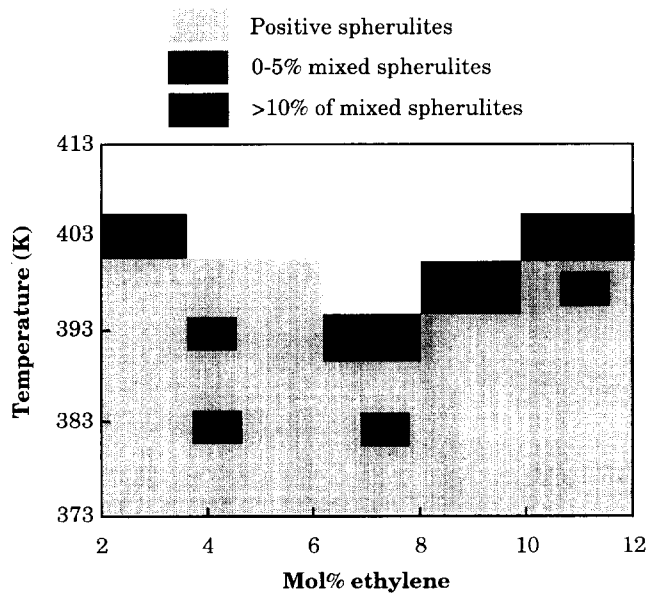
**Figure 9** Melting thermograms of copolymer with 8.7 mol% ethylene units after crystallization at 393 K for 130 min ( $3.5\times$  the half time crystallization) recorded at three different heating rates as shown in the figure

temperature melting peak is smallest for the sample with the lowest  $\gamma$  crystal content and largest for the sample with the largest  $\gamma$  crystal content. The amounts of crystalline material formed during the cooling to room temperature for these samples are only 11% ( $T_c = 373\text{ K}$ ) and 30% ( $T_c = 393\text{ K}$ ). The conversion of the  $\gamma$  form to the  $\alpha$  form revealed by WAXS (*Figure 7*) should affect the relative sizes of the two melting peaks as recorded at  $10\text{ K min}^{-1}$  heating rate. *Figures 8* and *9* present melting thermograms of samples of known initial content of the  $\gamma$  form recorded at different heating rates. The relative size of the low temperature peak as recorded at  $10\text{ K min}^{-1}$  was generally not in accordance with the  $\gamma$  crystal content at  $T_c$ : 50% at 383 K and 62% at 393 K. An increase in the scanning heating rate caused an increase in the relative size of the low temperature peak and, most important, the bimodal character of the melting was preserved (*Figures 8* and *9*). The relative size of the low temperature peak as recorded at  $40\text{ K min}^{-1}$  was in both cases in fair agreement with the  $\gamma$  form content. The conversion of the  $\gamma$  form to the  $\alpha$  form is according to Pae<sup>19</sup> prevented by sufficiently rapid heating.

Isothermal crystallization between 373 and 403 K led dominantly to the formation of positive spherulites, i.e. spherulites with a maximum refractive index along the spherulite radius. Some of the spherulites showed only weak birefringence and some spherulites consisted of regions of both negative (maximum refractive index in the perpendicular direction to the spherulite radius) and positive birefringence. The latter are referred to as mixed spherulites. Crystallization at low temperatures, which always led to the formation of positive spherulites, started with the formation of a relatively compact circular or elongated structure ('quadrites'). Crystallization at higher temperatures led to positive or mixed spherulites with a more fibrillar character and an irregular boundary to the surrounding melt (*Figure 10a*). Most of the spherulites growing at the higher temperatures, between 383 and 403 K, deviated from the circular habit and consisted of a central region of typically positive birefringence or



**Figure 10** Polarized photomicrographs of: (a) copolymer with 6.6 mol% ethylene units at 403 K; (b) copolymer with 5.9 mol% ethylene units at 388 K. The arrow indicates a ring-shaped demarcation line between weakly and strongly birefringent material



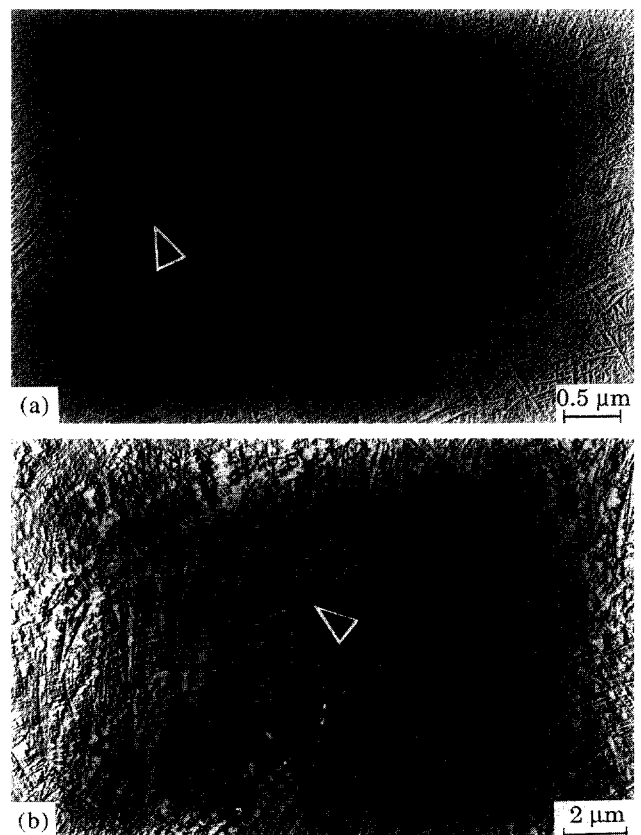
**Figure 11** Supermolecular structure as a function of ethylene-content and crystallization temperature

less commonly weakly positive or mixed sign. The peripheral parts of the fully grown spherulites were however always positive.

A remarkable ring structure was an occasionally occurring feature of the spherulites of the copolymer samples (Figure 10b). The ring constituted a demarcation line between weakly and more strongly positive birefringence and it was formed during the isothermal period. The ring structure was more common in the larger spherulites and it appeared most frequently (frequency: 30–50% of the spherulites) in the copolymers with 2.7, 5.9 and 8.7 mol% ethylene. More diffuse changes in magnitude of the birefringence along the spherulite radius appeared occasionally in spherulites with no clear ring structure. It is possible that the ring structure is due to a minor variation in ethylene content in different molecules and thus is indicative of fractional crystallization.

Figure 11 presents a summary of the morphology as revealed by polarized light microscopy. Crystallization at the lower temperatures led to the formation of positive spherulites. There was a clear trend at the higher temperatures for the formation of mixed spherulites. Negative spherulites were not observed in any of the samples.

Figure 12 presents electron micrographs of two copolymer samples crystallized at 393 K in contact with biaxially stretched Mylar<sup>®</sup> showing the characteristic lamellar structure of the  $\alpha$  crystals, the cross-hatching with an angle of 80° between the lamellae. Both straight and slightly curved crystal lamellae are also present. The

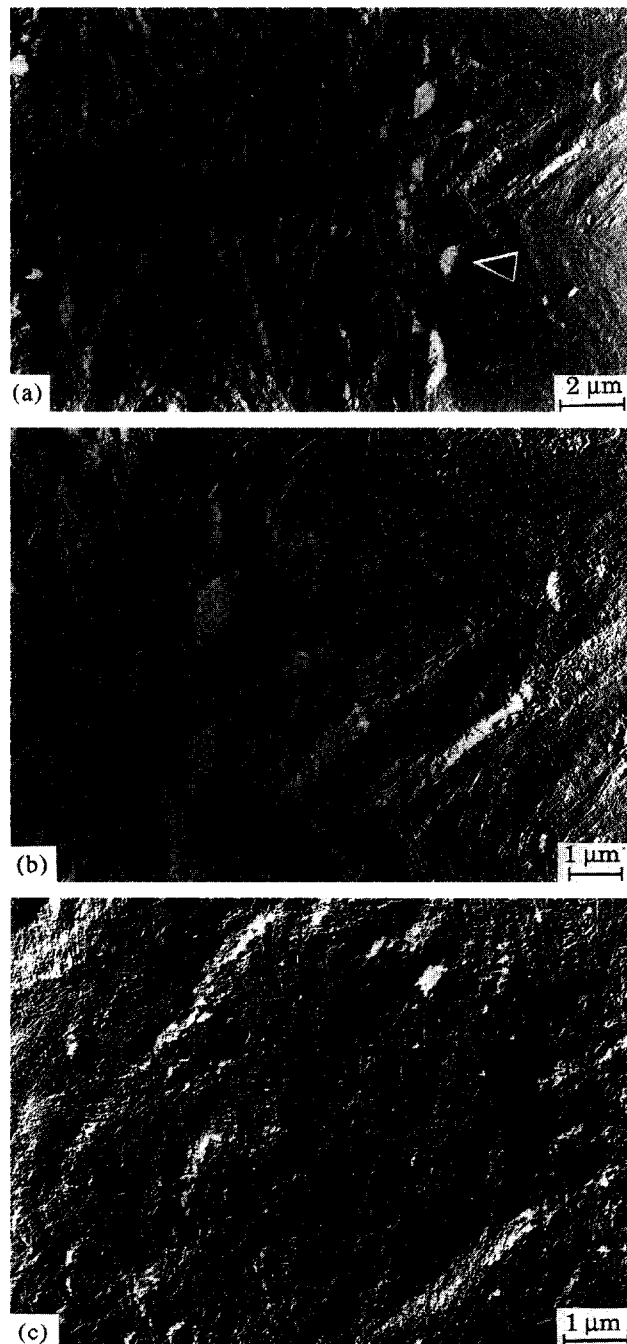


**Figure 12** Transmission electron micrographs of replicates of samples crystallized in contact with Mylar<sup>®</sup> and treated with permanganic acid: (a) copolymer with 2.7 mol% ethylene crystallized at 393 K for 20 h; (b) copolymer with 8.7 mol% ethylene crystallized at 393 K for 18.5 h. The arrows show low-angle lamellar branches

curvature is more pronounced in the sample with a higher ethylene content (cf. Figures 12a and b). It was shown by Campbell *et al.*<sup>20</sup> that cross-hatching was not present in samples consisting of pure  $\gamma$  crystal form. The coarse nature of the cross-hatched morphology is another characteristic feature of these samples. Occasional branching at much smaller angles, 15–40° was observed (Figure 12). Low-angle branching resulting in an angle of 45° between the lamellae has been reported for samples with coexisting  $\alpha$  and  $\gamma$  crystal form<sup>21</sup>. However, branching and splaying are features occasionally

appearing in homopolymers with exclusively  $\alpha$  crystal form<sup>22</sup>.

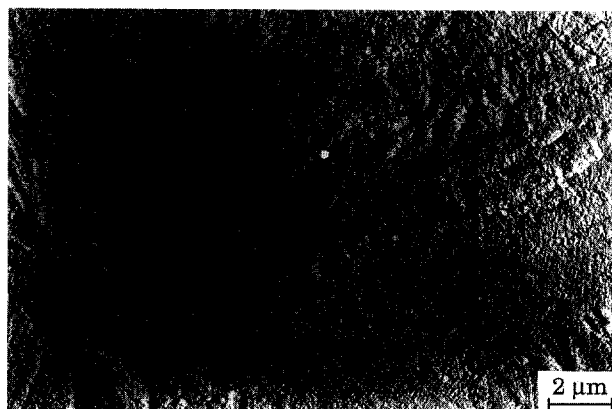
Crystallization at 373 K led to a finer cross-hatched morphology (Figure 13). This difference in lamellar morphology may be associated with the higher  $\alpha$  crystal content in the samples crystallized at 373 K (Table 2). It is also possible that the contact with the Mylar affected that coarseness of the cross-hatched structure. The fractional area of cross-hatched structure was essentially the same in samples with very different  $\gamma$  crystal content (0–49%, Figures 12 and 13) which indicates that the  $\gamma$  crystals are well dispersed in the matrix of cross-hatched  $\alpha$  crystals. The cross-hatched structure was more regular in the homopolymer than in the copolymer samples (cf. Figures 11–14). In some of the copolymer samples, spherical features, probably consisting of low-crystalline material, more susceptible to the etchant were observed (Figure 13a). The spherical shape indicates that phase separation occurred in the molten state prior to crystallization. The sample with 11.7 mol% ethylene units showed more curved lamellae (Figure 15) than the other copolymer samples. Curved lamellae have been observed in low molar mass homopolymer<sup>20</sup> and in highly atactic polymer<sup>21,23</sup> and is, according to Lotz *et al.*<sup>21</sup>, linked to the presence of  $\gamma$  crystals. Campbell *et al.*<sup>20</sup> observed



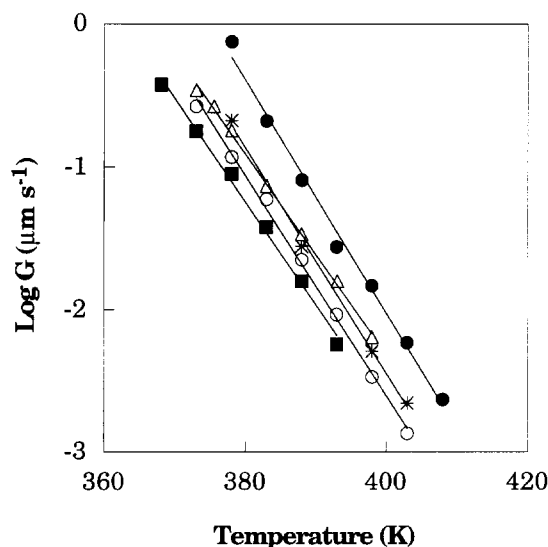
**Figure 13** Transmission electron micrographs of replicates of samples treated with permanganic acid: (a) and (b) copolymer with 2.7 mol% ethylene crystallized at 373 K for 20 min; (c) copolymer with 5.7 mol% ethylene crystallized at 373 K for 20 min. Both replicates were obtained from the bulk of melt-crystallized samples. The arrow in (a) indicates a spherical shaped feature which was etched out



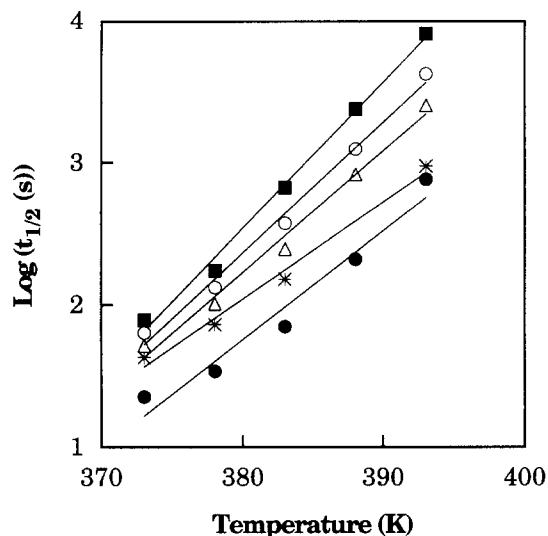
**Figure 14** Transmission electron micrograph of replicates of a homopolymer sample treated with permanganic acid. The sample was obtained from the bulk of a melt-crystallized sample



**Figure 15** Transmission electron micrograph of a replicate of copolymer with 11.0 mol% ethylene crystallized at 373 K for 20 min treated with permanganic acid. The sample was obtained from the bulk of a melt-crystallized sample



**Figure 16** The logarithm of the linear growth rate as a function of crystallization temperature for samples with different ethylene contents: ●, 2.7 mol%; \*, 5.7 mol%; ■, 6.9 mol%; △, 8.7 mol%; ○, 11.0 mol%



**Figure 17** The logarithm of the time to reach 50% of the final crystallinity as a function crystallization temperature for samples with different ethylene contents: ●, 2.7 mol%; \*, 5.7 mol%; ■, 6.9 mol%; △, 8.7 mol%; ○, 11.0 mol%

curved lamellae in high molar mass isotactic polypropylene rich in  $\gamma$  crystal form after crystallization at elevated pressure. Olley and Bassett<sup>22</sup> found slightly curved lamellae in the outer part of the spherulites of  $\alpha$  phase homopolymer crystallized at 420–430 K. The inner of the spherulites consisted of quadrites, i.e. aggregates of cross-hatched lamellae. The curved lamellae of the sample shown in *Figure 15* are uniformly distributed through the sample, a fact which suggests that these crystals are enriched in  $\gamma$  phase.

The linear growth rate data shown in *Figure 16* fall on lines essentially parallel-shifted along the temperature axis. Distinctly negative spherulites were not found at any of the temperatures. The morphology ranged from positive to mixed spherulites. None of the lines show any clear tendency for a kinetic transition, as was observed by Monasse and Haudin<sup>9</sup> at about 400 K for a copolymer

with 4.1 mol% ethylene units. However, the number of data points at temperatures above 400 K is too small to establish a break in the curve. It may thus be concluded that the majority of the data are, using the nomenclature of Clark and Hoffman<sup>10</sup>, associated with regime III growth. The shift along the temperature scale may thus be associated with a 10 K shift in the equilibrium melting temperature associated with the change in ethylene content from 2.7 to 11.0 mol% (*Figure 16*). Crystallization kinetics data obtained by d.s.c. (*Figure 17*) were generally in accordance with the linear growth rate data. The crystallization rate of the copolymer with 6.9 mol% ethylene units is significantly lower than the general trend given by the other copolymer samples. This particular sample also showed the lowest equilibrium melting temperature and the highest  $\gamma$  form content of all the samples studied.

## CONCLUSIONS

The inclusion of ethylene co-repeating units in isotactic polypropylene (0–11.0 mol% ethylene) led to approximately linear decreases in the kinetic and equilibrium melting temperatures and in  $T_g$  with increasing ethylene content. X-ray scattering showed that the content of the  $\gamma$  form increased with increasing ethylene content, increasing crystallization temperature and decreasing cooling rate. It was shown for one of the copolymers (8.7 mol% ethylene) that during heating approximately 50% of the  $\gamma$  form was converted to the  $\alpha$  form before the final melting of the sample. The rest of the  $\gamma$  crystals melted directly without being transformed into the  $\alpha$  crystal form. The multimodality of the crystal melting above the crystallization temperature in polymers with a more uniform crystal structure was caused by recrystallization during heating, whereas polymers with appreciable contents of both  $\alpha$  and  $\gamma$  forms exhibited multimodal melting at all the heating rates adopted. The relative size of the low temperature melting peak as assessed at a 40 K min<sup>-1</sup> heating rate was approximately proportional to the initial content of the  $\gamma$  form. The spherulitic structure of the copolymers was coarser than that of the homopolymer with internal and peripheral pockets of molten material during spherulite growth. The crystal lamellae exhibited more curvature in the copolymer samples than in the homopolymer.

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