On row-structures in sheared polypropylene and a propylene–ethylene copolymer

Robert H. Olley a,⇑, Geoffrey R. Mitchell a, b, Yasmin Moghaddam a

a Department of Physics, University of Reading, Whiteknights, Reading RG6 6AF, UK
b Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, Rua de Portugal – Zona Industrial, 2430-028 Marinha Grande, Portugal

Article info

Article history:
Received 5 August 2013
Received in revised form 20 December 2013
Accepted 14 January 2014
Available online 20 January 2014

Keywords:
Polypropylene
Copolymer
Nucleation
SEM (scanning electron microscopy)
WAXS (wide-angle X-ray scattering)
SAXS (small-angle X-ray scattering)

Abstract

The crystallisation of polymers such as polyethylene or polypropylene from the melt is greatly influenced by the flow-thermal history prior to the crystallisation. We explore the influence of the chemical configuration of polypropylene based chains on the formation of row structures on crystallisation. We use a combination of in situ time resolved small-angle X-ray scattering, ex situ wide angle X-ray scattering with optical and scanning electron microscopy to show that row nuclei are formed in random copolymers of propylene with a limited amount of ethylene subjected to modest shear flow fields. We contrast observations performed using two homopolymers of isotactic polypropylene and one random copolymer of propylene and ethylene. We propose that it is not strictly necessary to argue that the row nuclei are already crystalline nor to invoke epitaxial crystallisation as the mechanism for the nucleation of lamellae, as similar structures can be formed on carbon nanotubes and fibrils of dibenzylidene sorbitol. The combination of microscopy and scattering provides a powerful approach to investigating these phenomena, especially as compared to either technique used in isolation.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The crystallisation of polymers from stressed melts is of widespread interest both from a scientific viewpoint and from a technological processing perspective. The subject of crystallisation from stressed melts has been reviewed by Kumaraswamy [1] and more recently by Janeschitz-Kriegl [2], and one frequent occurrence in the time sequence of crystallisation from a stressed melt is the formation of row nuclei which give rise to structures known as “shish-kebabs”. In polypropylene such oriented structures may also grow on heterogeneous linear nuclei such as fibres by transcristallisation [3], for example in the case of in situ grown nanofibrils [4] or through the addition of nanoparticulates such as carbon nanotubes [5], whereas the presence of materials such as graphene nanosheets [6] may enhance the development of homogeneous row nuclei.

Polypropylene is the polymer best known for its remarkable propensity for forming row structures, but they are also found in polyethylene [7–9] as well as isotactic polystyrene [10], poly(phenylene sulfide) [11] and polylactide [12].

In polyethylene [7–9] and in polypropylene [13] the nuclei may be formed from a particular fraction of the polymer melt and in such cases it is well established that the generation of row nuclei is very dependent on the presence of a high molecular weight fraction or ‘tail’ in the polymers. Various models have been proposed, some depending on the coil-stretch transition [14,15], though alternative models exist such as [16]. Seki et al. have argued that row nuclei occur when there is sufficient of this HMW fraction to allow long-chain overlap [17]. Regardless of the mechanism of formation of the shish, it is understood that the kebab formation is a case of lamellar crystallisation on pre-crystallised fibres (shish) that serve as nucleation sites for the kebabs [18].

⇑Corresponding author. Address: Electron Microscopy Laboratory, J.J. Thomson Building, University of Reading, Whiteknights, Reading RG6 6AF, UK. Tel.: +44 (0)118 378 4616; fax: +44 (0) 118 378 4606.
E-mail address: R.H.Olley@reading.ac.uk (R.H. Olley).
Isotactic polypropylene, like most semi-crystalline polymers, crystallises from a quiescent melt in the form of spherulites but it readily assumes other geometries, crystallising from homogeneous row nuclei to form row structures or cylindrites, or from heterogeneous surfaces to give transcrystalline layers [19]. Row structures or cylindrites are easily generated by first shearing the melt, and can form in a range of number densities, ranging from isolated ones whose development can be followed easily under the optical microscope to very dense parallel arrays where the individual structures cannot be discerned optically. In polypropylene, a high tactility index has been found favourable to the development of shish-kebabs [17]. This raises questions as to the polymer attributes required to form row nuclei. Some work has been performed on blends of medium molecular weight branched polyethylene with a minority component of high or ultra-high molecular weight linear polyethylene (ethylene homopolymer). There the high molecular weight linear component has been observed to template the growth of the branched polyethylene [8,15]. However, we are not aware of any work where a copolymer by itself has been shown to form row structures, whether this be a majority ethylene or a majority propylene copolymer. This work compares the behaviour of two propylene homopolymers with that of a propylene–ethylene copolymer to explore the effects of the copolymerisation on the formation of row nuclei and subsequent templated lamellar growth.

2. Materials

Three polypropylene based materials were employed in this study, all supplied by Borealis, Finland and the characteristics are detailed in Table 1. As a ‘reference’ material we used a high-crystallinity homopolymer polypropylene HCPP with high tacticity. We compared this reference material with a second homo-polymer (ZNPP) prepared using Ziegler–Natta technology and which exhibits a lower tacticity and weight average molecular weight. The third material is a random copolymer (RACO) based on propylene with 5.1 wt% ethylene as comonomer. In terms of the melt flow index HCPP and RACO are very similar whilst the ZNPP system is substantially higher.

3. Experimental methods

3.1. Small-angle X-ray scattering

Time-resolving small-angle X-ray scattering (SAXS) measurements were made using the intense flux available on the fixed wavelength beamline 16.1 at the Daresbury Synchrotron Radiation source. Scattering data were collected using the Rapid Area Detector System with a time-cycle of 10 s. The scattering geometry was calibrated using a wet collagen fibre. The in situ small-angle X-ray scattering measurements employed a parallel plate shear cell equipped with mica windows, specially designed to facilitate in situ time-resolving X-ray scattering measurements [20]. A schematic of the shear cell and scattering geometry is shown in Fig. 1. The rotating plate consists of a stainless steel tri-spoke arrangement covered with a thin mica disc (0.03 mm in thickness), which allows the incident beam to pass unhindered for 85% of each revolution. An upstream synchronised rotating mask, fabricated from lead, minimised the background intensity for the period of a revolution when a spoke would have intercepted the incident beam. The fixed plate consists of a stainless steel plate with a single chamfered hole covered with a thin mica disc. The shear cell was equipped with electrical heating and cryogenic gas cooling system which allowed the sample temperature to be controlled and varied at set rates. The geometry of the cell was such that the incident beam was normal to the flow direction and parallel to the velocity gradient.

In this work, each sample was subjected to a defined temperature/shear flow cycle and an example is shown in Fig. 2. The design of the shear cell enabled X-ray scattering data to be obtained throughout the cycle. The specific cycle shown here contained the following stages: (a) heating from room temperature to 192.4 °C at a rate of 20 °C/min; (b) held at 192.4 °C for 5 min; (c) cooled to room temperature at a rate of 10 °C/min. When the sample reached a selected temperature, Tc, a shear rate of 20 s⁻¹ was applied for 25 s, giving a total of 500 shear units. During the shearing period, the sample continued to cool and over the shearing period the temperature dropped by 4.2 °C. After cessation of shear, cooling continued to below room temperature, after which the sample was removed from the shear cell. The 10 s data accumulation cycle used throughout the heating cycle gave a temperature variation of ~1.7 °C for each recorded scattering pattern. Samples for use in the shear cell were pre-moulded into discs 1 mm in thickness and 19 mm in diameter in the melt using a simple metal mould and hydraulic press.

3.2. Ex situ wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) data were obtained for processed samples at room temperature using two different approaches. The first used a flat plate Rigaku/MSC Saturn 92 CCD camera with a Rigaku FR-D rotating anode generator.

In the second method, intensity data were recorded as a function of 2θ at a fixed value of |Q| range using a symmetrical transmission diffractometer equipped with a graphite monochromator and pinhole collimation and a Cu Kα X-ray source where 2θ is the angle between the symmetry axis of the sample and the scattering vector Q and |Q| = 4πsinθ/λ, where λ is the incident wavelength and 2θ is the scattering angle. This instrument allowed a map of the undistorted reciprocal space in contrast to the limitations of a flat
detector fixed geometry system. Samples were mounted on the diffractometer so that the WAXS data were collected from a volume at the same radius of the disc as the SAXS data. As a consequence both sets of data relate to the same shear rate during the shear phase.

3.3. Microscopy

For microscopy, processed samples were etched for 1 h using the permanganic based mixture consisting of a 1% (w/v) solution of potassium permanganate in an acid mixture of 10 vols concentrated sulfuric acid, 4 vols orthophosphoric acid (85%) and 1 vol water. The etching procedures described in [21] were employed. Specimens were sputter coated with gold for examination by the following two microscopic techniques.

The first technique was based on a reflecting microscope setup for differential interference contrast, or Nomarski microscopy [22]. This enables a view of large areas which can only be observed piecemeal under the SEM. Moreover, it gives strong contrast for small variations in surface height, of the order of hundreds of nanometres, helped by the gold coating. The second technique involved the use of scanning electron microscopy operating in high vacuum mode at 20 kV using a Cambridge Stereoscan 360 SEM with a tilt angle of 35°.

4. Results

4.1. Small-angle X-ray scattering

In this section, SAXS patterns are displayed for the three materials studied, namely HCPP (Figs. 3 and 4), RACO (Figs. 5 and 6), and ZNPP (Figs. 7 and 8). The first figure in each pair contains a sequence of patterns as they develop from a single shearing temperature, the second figure shows the pattern from the end product of a range of shearing temperatures. Starting with HCPP, Fig. 3 shows a selection of SAXS patterns obtained during a particular time-resolved experiment of the type shown in Fig. 2. These are displayed in conjunction with the calculated invariant $\Omega$ and its derivative $d\Omega/dT$.

In each experiment, there are two important parameters, $T_s$, the temperature at which shearing was initiated and $T$ the temperature of the measurement. In this particular experiment $T_s = 138.5$ °C. The sequence of data shown in Fig. 3 starts at a point after the application of the shear flow pulse. As the temperature drops at a constant rate of 10 °C min$^{-1}$, intense scattering appears as spots or lobes along the meridional axis which is parallel to what was the flow axis. The intensity of these lobes initially grows but after reaching a maximum at $\sim 107$ °C, it falls continuously although it is always above the value shown in the
melt. This type of anisotropic pattern is typical of a semi-crystalline polymer in which the scattering arises from stacks of crystalline lamellae separated by regions of amorphous material. The position of the lobe in terms of $|Q|$ provides information of the so-called long period, which is the thickness of the lamellar plus the amorphous layer. The localisation of the scattering along the meridional axis reveals that these lamellae are preferentially arranged normal to the flow axis. The arrangement arises as a consequence of the formation during the flow phase of row nuclei which are aligned parallel to the flow axis and template or direct the growth of the chain folded lamellae perpendicular to the row nuclei. At commencement of shearing, at $T \sim 137\, ^\circ C$ (first pattern), the pattern has not changed noticeably from the original melt at $190\, ^\circ C$. The small spikes around the beam stop arise from the shear cell itself and do not relate to the sample. A significant amount of oriented scattering has become visible at $T \sim 130\, ^\circ C$ (second pattern) in the form of a vertical streak with a horizontal FWHM of $\sim 0.002\, \AA^{-1}$. On reaching a temperature of $118.9\, ^\circ C$, the oriented growth has become considerably more pronounced, and there is some lateral growth in terms of broadening the central streak. As the specimen cools still further, a ring arising from isotropic, spherulitic material develops, reaching maximum intensity near $102.6\, ^\circ C$.

We extracted a number of quantitative parameters from each of the small-angle X-ray scattering patterns. We have monitored the fraction of crystals by calculating the invariant $X$ given by

$$X = \frac{\int_0^{\sigma/2} \int_{Q_0}^{Q_{\text{max}}} Q^2 |I(Q)| \sin \sigma dQ d\sigma}{\int_0^{\pi/2} \int_{Q_0}^{Q_{\text{max}}} Q^2 |I(Q)| \sin \sigma dQ d\sigma}$$

which is directly related to the average of the square of the electron density differences; if the density difference between the crystals and amorphous is constant this is proportional to the volume fraction of crystals. We have calculated the derivative $dX/dT$ by fitting quartic functions to successive sets of points on the function $X(T)$ as shown in Fig. 3 and taking the analytical derivative of that function.

**Fig. 3.** A plot of the invariant, $\Omega$ and the derivative $d\Omega/dT$ against the experimental temperature $T$, derived from SAXS data for a sample of HCPP subjected to the temperature–shear–time profile described in the text with $T_s = 138.5\, ^\circ C$.

**Fig. 4.** SAXS patterns of HCPP recorded at $T = 89.5\, ^\circ C$ which have been subjected to a similar shear–temperature–time profile shown in Fig. 2 with the shear flow temperature $T_s$ indicated in the figure.
all the scattering intensities decrease in a roughly exponential way, a phenomenon already reported for polyethylene [24]. We attribute this to the fact that the difference in densities of crystalline and amorphous PP is reducing despite the increasing level of crystallinity, so giving a lower scattering intensity [25]. We have also plotted the derivative $d\Omega/dT$ which is a measure of the rate of crystal growth. The derivative of the invariant shows two peaks, at 122.5°C and 110.5°C (Table 2), these peaks are attributed to the maximum growth rate of the primary radial lamellae and of secondary, mostly crosshatched, lamellae.

Fig. 4 shows the small angle X-ray scattering patterns for samples prepared with different shear temperatures $T_s$. These patterns were obtained after cooling to a given temperature, in the case here 89.5°C where all specimens will have effectively crystallised fully. The advantage of using the patterns taken at this temperature is that the difference between densities of the crystalline and amorphous components is greater than at room temperature and hence the contrast is higher making observations more straightforward. At first sight, the specimens from the highest shear temperature appears to be isotropic, while for $T_s = 153.2$ °C there is a very slight azimuthal variation in the intensity. As the shear temperature decreases we observe a pair of lobes in the scattering pattern on the vertical axis, which we attribute to arrays of parallel lamellae growing from row structures. The mounting of the shear cell is such that any row nuclei generated should be vertically oriented. Lamellae growing from these would have their plane horizontal, but the stack of lamellae would be one on top of another along a vertical axis, giving rise to vertically oriented scattering. These lobes become increasingly pronounced as the shearing temperature is reduced to 138.5 °C in approximately 5°C steps.

The increase in orientation with lower shear temperature is as expected, since the row nuclei formed during shearing would be more stable at the lower temperatures, and also have less time to melt out before reaching the temperature of crystallisation onset. However, the pattern from lowest shearing temperature 128.7°C is again less pronounced, and reasons for this will be discussed according to evidence from microscopy.

For the specimen prepared with $T_s = 158.1$ °C, the pattern takes the form of an isotropic ring which does not reveal any preferred orientation of the lamellar crystals. Nevertheless, SAXS patterns recorded during cooling for this specimen did display some orientation. At $T = 110.7$ °C the pattern contained both isotropic and anisotropic scattering features which arise from different nucleation processes, and at that temperature they appeared equally weighted. At 102.3°C, the non-oriented growth had greatly increased and come to completely dominate the pattern. This suggests that growth from
row nuclei manifests itself much earlier than growth from point nuclei. Further consideration requires careful consideration of geometry. Firstly, the cylindrical growth from a row nucleus will occupy space much more rapidly at first. Secondly, because of the ideally isotropic growth from a collection of point nuclei, these will give rise to a ring of lower intensity than the sharper reflections from mutually oriented row nuclei. So in the final specimen, the pattern is indicative of very few row nuclei indeed.

Fig. 5 shows the sequence for a sample of RACO with $T_s = 123.8^\circ C$. Compared to HCPP, the whole process of crystallisation is shifted to lower temperatures. The maximum rate of crystallisation is lower and only one peak is observed in the derivative at $\sim 94^\circ C$. Fig. 6 shows the patterns of different RACO discs, sheared at different temperatures, in a similar manner to those shown in Fig. 4. Again, the orientation goes through a maximum at a certain shearing temperature, in this case 123.8 °C. There is what appears to be a small peak in the derivative at about 120°C; this may be due to the appearance of the row structures themselves. Most notable is the single crystallisation peak in the derivative (see also Table 2). This can be related to the structure of RACO being uniformly cross-hatched throughout development [26], rather than there being a dominant-subsidiary lamellar structure as in HCPP, where the secondary lamellae are observed to be lower-melting [27].

In the specimens taken as group, we see a similar pattern ascribable to progressive growth of lamellae on the row structures as was seen in the HCPP system. However, especially at $T_s = 128.7^\circ C$ and 123.8 °C, there is also a hint of equatorial scattering in the pattern, which could be related to cross-hatching development. Previous microscopic work has shown that the appearance of cross-hatched lamellae is initially sporadic, so the spacing is much wider and the $q$ value less [26].

Fig. 7 shows a plot of the invariant, $\Omega$ and the derivative $d\Omega/dT$ against the experimental temperature $T$, derived from SAXS data for a sample of ZNPP subjected to the temperature–shear–time profile described in the text with $T_s = 138.5^\circ C$.

Table 2

| Polymer | Maximum of invariant with respect to temperature °C | Maxima of derivative of the invariant with respect to temperature °C |
|---------|---------------------------------------------------|----------------------------------------------------------------------------|
| HCPP    | 106                                               | 122.5                                                                     |
| RACO    | 84.5                                              | 93.5                                                                      |
| ZNPP    | 96.5                                              | 115                                                                        |

Fig. 8. SAXS patterns of ZNPP recorded at $T = 89.5^\circ C$ which have been subjected to a similar shear–temperature–time profile shown in Fig. 2 with the shear flow temperature $T_s$ indicated in the figure.
HCPP; the maximum in the invariant $\Omega$ also occurs about 10$^\circ$ lower (Table 2). Fig. 8 shows the SAXS patterns recorded for ZNPP discs with different values of $T_s$; these appear to correspond most closely to the HCPP sample with $T_s$ roughly 10$^\circ$ higher, and somewhat less oriented.

Looking at all three materials, as crystallisation proceeds through cooling, the SAXS pattern moves to a larger $Q$ value as the density of lamellae forming on the row nuclei increasing with time. At the highest temperatures of shearing, the SAXS patterns at $T_s = 89.5$ °C show an isotropic distribution of the scattering. In other words, the shearing does not result in the formation of row nuclei, or else these row nuclei are either redissolved or become randomly aligned.

4.2. Ex situ wide-angle X-ray

We have used ex situ wide-angle X-ray scattering to evaluate the distribution of crystal orientation, or more precisely the distribution of the orientation of crystal planes in the final room temperature samples. The crystal structure of the three polymers is dominated by the $\alpha$-form, and the reflections due to this are chosen to assess the level of preferred orientation of the crystal planes. Microscopic observation (below) does reveal the presence of some $\beta$-form, but it is not present in sufficient proportion to contribute significantly to the diffraction patterns. As a reference to the $\alpha$-form, Fig. 9a shows the WAXS pattern for a compaction made of highly aligned fibres of iPP [28]. This shows the classic fibre diffraction pattern for iPP with the fibres mounted in the vertical direction. The original fibres would show very high orientation indeed, and only equatorial 110 reflections. However, in the compaction process a small amount of material has melted and recrystallised in the crosshatched form, so extra 110 arcs at roughly 80$^\circ$, almost meridional, are seen, but at much lower intensity than is seen for spherulitic PP. The 040 reflection relates to the common $b$-axis, and so one arc is common to both the main and crosshatched lamellae. Fig. 9b shows the WAXS pattern for the HCPP specimen sheared at 138.5 °C, mounted so that what was the flow axis is vertical and the volume of material examined was the same as in the earlier SAXS experiment. It is immediately clear that the orientation distribution of the crystal planes is broader than in the fibre pattern as is evidenced by the azimuthal arcing of the reflections. The meridional 110 reflections are much stronger relative to the equatorial ones (90$^\circ$ and 270$^\circ$) than parent lamellae. We suggest that with these, a greater proportion of the lamellar material is set for the specific diffraction conditions, than is the case with the parent lamellae.

4.3. Microscopy

The X-ray scattering results so far have all been taken from one particular distance from the centre of each specimen, which corresponds to a specific shear rate. However, with microscopy one can, by working along the radius, also study the variation of morphology resulting from differing shear rates, which increase linearly from the centre of a specimen. We used both optical and electron microscopy to explore this spatial variation.

Fig. 11 shows images taken with the interference microscope of the specimen sheared at $T_s = 148.3$ °C. Fig. 11(a)
shows an area ~6 mm from the centre with what was the flow axis vertical on the page. Starting from the outside (right of picture), one sees the densely packed row morphology which extends to the edge of the disc, to an optically brighter band in the middle. This shows rows a few μm apart, but particularly significant about the brightness is that it suggests a greater uniformity of organisation in this region, especially in regard to the $g^\parallel$ outward...
growth direction. At left of picture, towards the centre, well-separated row structures are observed in a largely spherulitic matrix. What is significant here is that as the shear rate and therefore the shear strain varies linearly across the radius, it reveals that there is a critical value of shear parameters (rate or overall strain) that leads to a much greater development of row structures, as observed previously in polyethylene [7]. Fig. 11b shows a region 3 mm from the centre, with isolated row structures in a spherulitic matrix. The SAXS data were recorded from a volume position further to the right of the image shown in Fig. 11a.

In Fig. 12, observations of similar HCPP specimens under the SEM, taken from about 2 mm in from the edge, roughly equivalent to the position of the X-ray beam, correspond to the optical pictures and deductions from the SAXS data. Fig. 12a shows the most highly oriented specimen \((T_s = 138.5 \, ^\circ C)\) shows densely packed row structures. In Fig. 12b there are some features standing out, which we know from experience with row structures generated from molten pellets and in injection moulded specimens, as well as from work of other authors [31,32] are what look like lamellar stacks of the \(\beta\)-form, though strictly speaking they are not stacks of individual lamellae but hedrites observed perpendicular to their axes [33]. Although in many Ziegler–Natta PPs \(\beta\)-spherulites form from the unperturbed melt, HCPP hardly ever develops the \(\beta\)-form. The presence of this form is generally much more pronounced with row structures: for example in what appears to be a very similar system using the same shear cell, where transcristallisation occurs on oriented fibrils of dibenzylidene sorbitol [4], this form has not been observed. This distinction was
most pronounced in a reported work, where only the α-form was observed growing on a quiescent fibre, while if the fibre was gently pulled in the melt, the β-form grew from row structures generated next to the fibre surface [3]. Fig. 12c shows at sufficiently high shearing temperatures (158.1 °C and above) row structures either do not form or are sufficiently transient not to survive cooling to a practical crystallisation temperature. Fig. 12d shows that at a temperature roughly 10 °C below the optimum for row development (128.7 °C) there is considerable development of spherulites again appear, suggesting that they were nucleated before the shearing started. This is in agreement with the somewhat lower orientation of this specimen observed by SAXS and WAXS.

Fig. 13 shows SEM micrographs of RACO. Sheared at high temperature, 163 °C (Fig. 13a), the specimen looks rather like an unsheared one, being indistinguishable from the morphology of such specimens as intensively studied under TEM [26]. It shows at high contrast thin objects of about 5 µm in length, which are observed both isolated and in groups in what appears to be a rather featureless matrix. However, these TEM studies have revealed that both appearances are due to the same kind of object, namely the early growth stages of crystalline PP called quadrites, consisting of practically equal amounts of lamellae in either of two fast growth orientations generated by cross-hatching, and sharing a common β-axis, and considerably thinner in the dimension along that axis. How they are revealed by etching depends on the orientation of the common β-axis – if it lies close to the plane of the etched surface, then the quadrites are revealed edge-on, and in sharp contrast. If a quadrite is seen looking down the β-axis then the surface rugosity is much less, and in the case of PP copolymers it requires TEM [26] or AFM [34] to clearly reveal the surface structure. Because of the large number of specimens being studied, we did not undertake TEM studies with any of them. The specimen sheared at 123.8 °C (Fig. 13b) shows some row structures but these are still largely surrounded by the typical unsheared morphology. No β-crystalline material is observed: it has been reported that even in the presence of a β-nucleating agent the incorporation of comonomer units (roughly half the quantity in RACO) considerably reduces the tendency to β-crystallisation, and that, unlike in the homopolymer, there is no temperature range in which the β growth rate does not exceed that in the α-form [35]. A specimen sheared at 114.0 °C (Fig. 13c) is most densely packed with row structures. The lowest shear temperature applied to this specimen was 104 °C (Fig. 13d), and here there are much fewer row structures, while there are many clusters of isolated quadrites seen among the row structures. Here we have competition between generation of row structures in shear, growth of these row structures, and growth of quadrites which may have started to nucleate while or even before shear was applied.

Fig. 14 shows the morphology of ZNPP specimens. Sheared at the highest temperature, 167.9 °C (Fig. 14a) the morphology is entirely spherulitic. In the view of the specimen sheared at 128.7 °C (Fig. 14b) two well developed row structures are seen, surrounded by a spherulitic matrix. The two fan-shaped objects in bright contrast are β-crystalline hedrites which as described above often arises in row structures. The low nucleation density both of rows and spherulites allows these to develop a more typical ‘axialitic’ fan structure due to the usual branching mechanism of spherulites [36], which the β-material can
do here because at this temperature it has a faster growth rate than the majority of \(\alpha\)-spherulitic material and can grow ahead and colonise areas of uncrystallised melt [31]. Two views (Fig. 13c and d) of a specimen sheared at 118.9\(^\circ\)C show much development of row structures, with a much more extensive development of the \(\beta\)-form than in HCPP. Both views show a few isolated spherulites which must have started to develop before the onset of shear.

5. Discussion

5.1. Basic behaviour of the polymers

An undisturbed, relaxed polypropylene melt, not containing an added nucleating agent, will generally form spherulites on cooling from the melt. The presence of row structures is an indication that the melt is not totally relaxed, but at the time of crystallisation retained some memory of flow. The most commonly observed presence is in injection moulded articles, where they tend to form near the surface close to where shearing of the melt is at maximum.

They are also potentially present in commercial pellets before moulding. However, they do not manifest themselves until the pellet is melted at not too high a temperature, typically 170–200\(^\circ\)C, and then allowed to recrystallise. From such experiments one can determine that whatever gives rise to them decays with time in the melt, typically over minutes, and more quickly at higher temperatures. Pellets are prepared from an extruded melt, and their row structure precursors are probably produced under extensional flow, even the gentlest of which is able to produce row structures [13].

The presence of row nuclei will cause the material to crystallise at a higher temperature than from an equivalent melt without them. What has been observed optically by Varga [31], ourselves and others is how in a thin film in the microscope hot stage, the field rapidly fills with long birefringent rows, while at the same temperature, if the row nuclei are completely melted out beforehand, the field fills much more slowly with spherulites grown from isolated nuclei. In rows formed from remelted pellets, this can require remelting tens of degrees above any observable crystallisation temperature, but in the present work, rows generated by shear are formed at somewhat lower temperatures, at which crystallisation might be observed but only after waiting for some hours. This behaviour is related to the self seeding process, where similar enhancement of crystallisation rate can be followed by thermal analysis [37].

If row nuclei are very densely packed, then row structures are seen to have filled space before any significant amount of spherulitic growth could start. However, at the higher shearing temperatures observed here, competition is seem to take place between the two forms of growth. Comparing row nuclei with a given distance apart and heterogeneous point nuclei with the same spacing, the row structures with their cylindrical form will initially generate more crystal than the array of small spherulites, but the difference in rate will decrease with time until space is filled. However, at higher shearing temperatures where the row structures are more widely spaced, the comparatively closer spacing of heterogeneous nuclei which remains unaffected will ensure that spherulitic growth dominates.

As observed during their development in the hot stage optical microscope, PP row structures do indeed appear...
very cylindrical. One might thus consider that the row nuclei, while the molecular chains are aligned giving rise to a unique \(c\)-axis, might approximate to an idealised cylindrical symmetry. However, close electron microscopic observation of row structures in a similar PP homopolymer, formed and crystallised at 140 °C [13], shows that there is a continuity of crystal orientation, over quite considerable length, of the lamellae which grow from the nuclei. Even so, the row structures do display a considerable approximation to cylindrical growth, attributable to localised discontinuities in the crystallography of the row nucleus itself, as well as occasional incoherent secondary nucleation which allows space-filling growth to start at non-crystallographic angles.

It was observed also [13] that in a low-tacticity fraction of homopolymer, which might behave similarly to the copolymer, the rows did not display incoherent secondary nucleation to such an extent, resulting in row structures with angular gaps in their outward growth profile. Nevertheless, the main feature that has been observed is that, without question, copolymers of this type form row structures just as readily as homopolymers.

Differences between the homopolymer HCPP and the copolymer RACO have already been characterised for spherulitic growth. In the homopolymer [27] the nucleus first develops into an object in which cross-hatching develops equally in both directions, but as growth proceeds the outward-growing lamellae with become increasingly dominant with distance from the nucleus, and the population of cross-hatched material increasingly smaller in proportion. In the copolymer likewise the initial object is cross-hatched, but the dominant lamellae must remain spaced out, the intervening space being filled by molecules with too high an ethylene content to crystallise at the chosen temperature [26].

In homopolymer row nuclei, the development of cross-hatching takes a different course from that in spherulites. The initial growth is made up of densely packed parallel stacks of lamellae, with no room for cross-hatching. As development proceeds, deviations of a few degrees from the initial direction of growth lead to increasing gaps between the primary lamellae, which are filled with cross-hatched material. However, this will lead to a limited development of cross-hatching, similar to that which is approached in the mature development of spherulites, but from the opposite direction. A similar development is observed in different types of polyethylene nucleated on ultra-high molecular polyethylene fibres, where lamellae are seen to be thinner and more densely packed close to the fibre itself, while further out fuller lamellar development is found, similar to that near the growth front of large spherulites [38]. The cited work also draws out contrast to spherulitic growth, where close to the nucleus lamellae have greater space for development and thickening by annealing compared with further out, where an array of dominant nuclei has established itself. With the copolymer, the initial lamellae will not be able to fill the space [39], so that cross-hatching can develop close to the nucleus.

In the homopolymer, very similar row structure arrays are produced in injection moulding, and their development has been time-monitored and observed under the electron microscope using a stopped-flow technique [40]. Although this is referred to as “shear-enhanced” nucleation, it is thought that the actual mechanism is one of extensional flow, since more than the minimum amount of shear will of itself introduce an extensional strain in any given element of the liquid. Indeed, using the gentlest of techniques, a small extensional deformation on the melt produces row structures suitable for electron microscopic observation [13]. So in the present work, extensional deformation of individual fluid elements is most likely to be the source of row nucleation, with the high molecular weight components of the materials, consisting of the molecules with the longer relaxation times [41] partly compensating for the weak extensional component of the flow. In a reported comparison of two materials, an increase of around 60% in polydispersity and weight average molecular weight leads to an order of magnitude increase in the viscosity-averaged relaxation time [42].

Especially in view of the fact that the copolymer also easily forms row structures, we attribute the observation that ZNPP forms a given density of row structures at temperatures roughly 10\(^\circ\) lower than the equivalent in HCPP to the lower \(M_n\) and presumably short high molecular weight tail of the ZNPP, rather than its somewhat lower tacticity.

Thus far, we have discussed the crystalline structure that forms from the row nuclei, or in the more colloquial description of “shish-kebab” growth, the structure of the “kebab”. This, however, is a different matter from the structure of the “shish” itself.

In the homopolymer, it is quite easy to envisage the row nuclei as aggregates of oriented molecules which have come side-to-side and formed a crystalline core. In polypropylene, this requires a specific orientation of helix direction with regard to the crystallography of the material. One slight difference from lamellar crystallisation is that in lamellae, helix direction can be selected on re-entry from a chain fold, whereas in the crystallisation of a bundle of oriented chains, each chain will, so to speak, have to wait until a suitable niche is found. The structure formed, however, does not necessarily have to display typical crystal facets. While the \(c\)-axis will naturally extend along the row length, observations [13] perpendicular to the row axis show that several different orientations of the \(g^*\) and \(b\)-axes are found in close proximity, so the row structure is roughly cylindrical in section, rather than lath-like as would obtain if strict crystallographic continuity were maintained. Indeed, the material in the row nucleus could be quite disordered as regards the \(g^*\) and \(b\)-axes, and exhibit only a crude form of crystallinity, with nucleation occurring by graphoepitaxy [43].

In the copolymer, there is the added difficulty of what to do with the comonomer units. In lamellar crystallisation, these are rejected from the crystal lattice and are concentrated in the amorphous material. However, this is not possible if an entire chain has to be contained in a crystal-line core. It is likely the ethylene units can be incorporated relatively easily, since they will not force an expansion of the crystal lattice, but give rise to vacancies where the missing methyl units would be. While thermodynamically unfavourable, this would be no more so than stems folding
at a lamellae interface, and so a depression of crystallisation temperature, consistent with what is observed here, should be sufficient for chain to crystallise and form a nucleus. Such might not necessarily be the case with butyl or higher comonomers, which would significantly expand the molecular weight fraction in the molecular weight distribution, and so need not be taken into account here [44]. Recent work [30] indicates that the presence of butene-1 comonomer leads to the production of γ-phase, which transforms to α on mechanical stretching of the fully crystallised material.

6. Conclusions

(1) This present study confirms the trend, previously reported by other workers, that the degree of formation of row structures in isotactic polypropylene homopolymer is related to the presence of high molecular weight fraction in the molecular weight distribution.

(2) The precursors to row structures are formed in a sheared melt, and can persist with relaxation times of several minutes. The phenomenon cannot simply be described as "shear-induced crystallisation", but is a distinct precursor to the crystallisation process.

(3) Row nuclei are also formed in random copolymers of propylene with a limited amount of ethylene. Therefore, if they crystallise before nucleating the lamellae that form on them, they will be quite defective in their crystalline lattice, in contrast to the so-called "extended chain" crystallisation of polyethylene at high pressure.

(4) It is, however, not necessary to invoke crystallisation of the row nuclei as necessary for the nucleation of lamellae, because transcrystralisation can occur on carbon nanotubes and fibrils of dibenzylidene sorbitol.

(5) The lamellar spacings of polypropylene in row structures are characteristic of whether the material is a homopolymer or copolymer, such as a characteristic of mature spherulitic growth. This feature is similar to that observed in crystallisation of different types of polyethylene as observed on ultra-high molecular polyethylene fibres, where the growth rapidly becomes characteristic of the material itself, rather than being dictated by the fibre.

(6) The combination of microscopy and scattering provides a powerful approach to investigating these phenomena, especially as compared to either technique used in isolation.

Acknowledgements

The synchrotron based studies were performed at the STFC Daresbury Synchrotron on beam-line 16.1 and we thank Anthony Gleeson for his help with the beam-line. The polymers were provided by Borealis Ltd. The electron microscopy was performed in the Centre for Advanced Microscopy at the University of Reading.

References

[1] Kumaraswamy G. J Macromol Sci C:Polym Rev 2005;45:375–97.
[2] Janeschitz-Kriegl H. Crystallisation modalities in polymer melt processing. Fundamental aspects of structure formation. Flow induced processes causing oriented crystallisation. Wien, New York: Springer; 2010 [Chapter 3].
[3] Varga J, Karger-Kocsis J. J Mater Sci Lett 1994;13:1069–71.
[4] Nogales A, Mitchell GR, Vaughan AS. Macromolecules 2003;36:4898–906.
[5] Chen YH, Zhong GJ, Lei J, Li ZM, Hsiao BS. Macromolecules 2011;44:3080–92.
[6] Xu JZ, Chen C, Wang Y, Tang H, Li ZM, Hsiao BS. Macromolecules 2011;44:2808–18.
[7] Popple JA, Mitchell GR, Sutton SJ, Vaughan AS, Chai C. Polymer 1999;40:2769–77.
[8] An Y, Holt JJ, Mitchell GR, Vaughan AS. Polymer 2006;47:5643–56.
[9] Kanayama T, Matsuba G, Ongeno Y, Nishida K, Shimizu HM, Shinohara T, et al. Macromolecules 2007;40:3650–4.
[10] Azzurri F, Alfonso GC. Macromolecules 2008;41:1377–83.
[11] Zhang R, Min M, Gao Y, Lu A, Xu Y, Huang Y, et al. Mater Lett 2004;60:293–8.
[12] Li XJ, Li ZM, Zhong GJ, Li LB. J Macromol Sci – Phys 2008;44B:511–22.
[13] White HM, Basset DC. Polymer 1998;39:3211–9.
[14] Zhu PW, Tung J, Edward G. Polymer 2005;46:10960–9.
[15] Hsiao BS, Yang L, Somani RH, Avila-Orta CA, Zhu LJ. Phys Rev Lett 2005;94:117802.
[16] Janeschitz-Kriegl H. Macromolecules 2006;39:4448–54.
[17] Seki M, Thurman DW, Oberhauser JP, Kornfeld JA. Macromolecules 2002;35:2593–94.
[18] Dukovski I, Muthukumar M. J Chem Phys 2003;118:6648–55.
[19] White HM, Basset DC. Polymer 1997;38:5515–20.
[20] Nogales A, Thornley SA, Mitchell GR. J Macromol Sci – Phys 2004;B43:1161–70.
[21] Shahin MM, Olley RH, Blissett MJ. J Polym Sci Polym Phys 1999;37:2279–86.
[22] Sections 5.4.1 to 5.7 in applied polymer light microscopy. Hemsley DA, editor. London: Elsevier Applied Science; 1989.
[23] Alexander LE. X-Ray diffraction methods in polymer science. New York: Wiley; 1979 [Chapter 5].
[24] Schouterden P, Vandermarliere M, Riekel C, Koch MHJ, Groeninkx G, Rejnaers H. Macromolecules 1989;22:237–44.
[25] Fischer EW, Kloos F, Lieser G. J Polym Sci Lett 2000;25:2763–9.
[26] Weng J, Olley RH, Basset DC, Jaaskekalinen P, J Polym Sci B: Polym Phys 2003;41:2342–54.
[27] Weng J, Olley RH, Basset DC, Jaaskekalinen P, J Polym Sci Phys Phys 2003;1:7:845–50.
[28] Hosier IL, Alfaro RG, Lin JS. Polymer 2004;45:3441–55.
[29] Varga J, Karger-Kocsis J. J Mater Sci 1994;13:1069–71.
[30] Fillon B, Wittmann JC, Lotz B, Thierry A. J Polym Sci B: Polym Phys 2000;38:672–81.
[31] Varga J. J Polym Sci Lett 1996;7:845–50.
[32] Weng J, Olley RH, Basset DC, Jääskeläinen P. J Polym Sci B: Polym Phys 2003;41:2342–54.
[33] Abo El Maaty MI, Bassett DC, Olley RH, Hine PJ, Ward IM. J Mater Sci 2003;38:2763–9.
[34] Dukovski I, Muthukumar M. J Chem Phys 2003;118:6648–55.
[35] White HM, Basset DC. Polymer 1997;38:5515–20.
[36] Nogales A, Thornley SA, Mitchell GR. J Macromol Sci – Phys 2004;B43:1161–70.
[37] Shahin MM, Olley RH, Blissett MJ. J Polym Sci Polym Phys 1999;37:2279–86.
[38] Sections 5.4.1 to 5.7 in applied polymer light microscopy. Hemsley DA, editor. London: Elsevier Applied Science; 1989.
[39] Alexander LE. X-Ray diffraction methods in polymer science. New York: Wiley; 1979 [Chapter 5].
[40] Schouterden P, Vandermarliere M, Riekel C, Koch MHJ, Groeninkx G, Rejnaers H. Macromolecules 1989;22:237–44.
[41] Fischer EW, Kloos F, Lieser G. J Polym Sci Lett 2000;25:2763–9.
[42] Weng J, Olley RH, Basset DC, Jaaskekalinen P, J Polym Sci B: Polym Phys 2003;41:2342–54.
[43] Abo El Maaty MI, Bassett DC, Olley RH, Hine PJ, Ward IM. J Mater Sci 2003;38:2763–9.
[44] Fillon B, Wittmann JC, Lotz B, Thierry A. J Polym Sci B – Polym Phys 1999;37:2279–86.
[45] Trifonova-van Haering D, Varga J, Ehrenfest GW, Vancio GJ. J Polym Sci Polym Phys 2000;38:672–81.
[46] Hosier IL, Alamo RG, Lin JS. Polymer 2004;45:3441–55.
[47] Varga J, Schulek-Tóth F. J Therm Anal 1996;47:941–55.
[48] Bassett DC, Vaughan AS. Polymer 1985;26:717–25.
[49] Fillon B, Wittmann JC, Lotz B, Thierry A. J Polym Sci B – Polym Phys 1993;31:1383–93.
[50] el Maaty MI, Bassett DC. Polymer 2005;20:9682–8.
[51] Zhao Y, Vaughan AS, Sutton SJ, Swingler SG. Polymer 2001;42:6509–608.
[52] Kumaraswamy G, Verma KK, Issaian AM, Wang P, Kornfeld JA, Yeh F, et al. Polymer 2001;42:6509–608.
[53] Mykhaylyk OY, Champong P, Impardice C, Fairclough JPA, Terrill NJ, Ryan AJ. Macromolecules 2010;43:2389–405.
[54] Pantani R, Balzano L, Peters GWM. Macromol Mater Eng 2012;297:60–7.
[55] Yan S, Bonnet M, Petermann J. Polymer 2000;41:1139–45.
[56] Gahlteiner M, Jääskeläinen P, Katajisto E, Paulik C, Reussner J, Wolfschwenger J, et al. J Appl Polym Sci 2005;95:1073–81.