Polymer 50 (2009) 5559–5564

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

A quantitative electron-microscopic investigation of α-phase lamellae in isotactic polypropylene fractions

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ARTICLE INFO

Article history:
Received 6 July 2009
Received in revised form
10 September 2009
Accepted 13 September 2009
Available online 25 September 2009

Keywords:
Polypropylene
Lamellae
Cross-hatching

ABSTRACT

Lamellar thicknesses and cross-hatching frequencies in α-isotactic polypropylene have been measured for two series of fractions using linear nucleation to provide large arrays of oriented lamellae in row structures for sampling. One series is of high tacticity polymers differing in molecular mass from $\sim 6 \times 10^4$ to $\sim 8 \times 10^5$, the other has low and high tacticity materials for $\sim 9 \times 10^4$ and $\sim 2 \times 10^5$ masses. These have allowed the differing influences of both molecular mass and tacticity to be evaluated. Lamellar thicknesses increase with molecular mass to $\sim 5 \times 10^5$ then level off. This is consistent with the fold surface increasing its free energy by ~20% for longer molecules as its structure becomes progressively more complex. Except for the lowest fraction, the thickness of cross-hatching lamellae is less than that of its radial neighbours because of differential thickening. The frequency of cross-hatching is greatest for the least tactic fraction but decreases linearly with molecular length. This dependence suggests that chain ends play a key role in initiation probably by laying down the first segment in epitaxial orientation. This suggestion could also account for the reduced thermal stability of spherulite centres and regions of high cross-hatching density where there is competition for chain ends between thickening and cross-hatching. The curvature of lamellae at the very end of a row mirrors the dependence of lamellae thickness with molecular mass and allows cilia pressure, the factor strongly involved in causing the lamellar divergence underlying spherulitic growth, to be estimated as ~100 Pa.

1. Introduction

This paper reports a quantitative study of the lamellar morphology of melt-crystallized isotactic polypropylene as functions of molecular length and tacticity undertaken for two principal reasons. On the one hand, the macroscopic properties of a crystalline polymer depend crucially on its inherently complex physical microstructure so that such knowledge provides a background to tailoring properties of commercial materials. On the other hand, there is the underlying fundamental issue of what additional properties are brought to polymeric crystallization by molecular length beyond those found for small molecules.

Most of our knowledge of the latter has come, logically, from studies of linear polyethylene and its oligomers which are the closest approach to the ideal flexible chain. The key factor is lamellar growth, which for longer molecules is accomplished by chainfolding, driven by the volume free energy reduction on crystallization of the internal molecular stems albeit partly offset by the additional surface contribution, then subject to the common but still mysterious process of isothermal lamellar thickening. For typical fast growth rates (Regime II for polyethylene) surface condition is a secondary issue leading to rough, less-well-ordered surfaces prone to subsequent reorganization. Only for slowest (Regime I for polyethylene) growth is there time for as-grown surfaces to achieve smooth ordering. In linear polyethylene it is the reorganization of rough surfaces towards the preferred smooth ones ({001} to {201} and the associated adoption of S-profiles) which is responsible for banded growth. More generally, as shown for linear-low-density polyethylene, reduction of surface stress drives banding [1].

Study of polypropylene can bring additional knowledge on two counts. First it is the simplest poly(α-olefine) $[CHCR]_n$, with $R = CH_3$, introducing tacticity into the aliphatic chain. We find, as is expected, that less tactic as well as shorter molecules are less able to crystallize and so segregate within the morphology although this is now known not to be the cause of spherulitic growth as was once proposed. Additionally and more importantly, the common α form of the isotactic polymer has a unique cross-hatched twinned

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0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.09.038

morphology in which chains change orientation across the twin plane by ~90° creating a distinct lamellar (cross-hatching) population and significantly affecting properties. Thus unlike most other polymers, including the β form of isotactic polypropylene, its spherulites do not have their highest melting point at their centres so that they melt from the outside in. On the contrary, isothermally-crystallized spherulites of α polypropylene melt in their centres before regions at greater radius [2,3]. This is because of the restriction imposed by cross-hatching on isothermal lamellar thickening which in other systems makes the oldest lamellae (at spherulite centres) the thickest and highest melting. There is the potential, therefore, of gaining further understanding of isothermal lamellar thickening and how it is inhibited.

With this background we report a fundamental study, using fractionated polymer, of lamellae in melt-crystallized α-isotactic polypropylene, investigating how molecular length and tacticity affect lamellae in both radial and cross-hatched orientations. Lamellar thicknesses and cross-hatching frequencies have been measured, *inter alia*, for a polypropylene homopolymer and fractions thereof as functions of crystallization temperature, molecular length and tacticity. It is shown that, at a given temperature, longer molecules form thicker lamellae, to an asymptotic limit, consistent with a corresponding increase in surface free energy. We now extend previous results which showed that cross-hatching lamellae are thinner than neighbouring radials for higher crystallization temperatures but the difference declines for shorter molecules and disappears for the homopolymer at 115 °C [4]. This equality also applies at all temperatures for fractions below molecular masses of $\sim 6 \times 10^4$.

The results not only provide a unique database of how molecules are distributed within the lamellar morphology but also reflect on molecular mechanisms. Thus the demonstration that the frequency of cross-hatching declines inversely with molecular length suggests that molecular ends are key to its initiation leading in turn to an explanation of the reduced thermal stability of spherulite centres. Moreover, the curvature of lamellae at the very end of a row allows an estimate of cilia pressure which is largely responsible for lamellar divergence and the formation of polymeric spherulites.

2. Materials and experimental

Table 1 lists details of the polypropylene homopolymer used, provided by Borealis Polymers Oy, and fractions separated from it. Those varying in molecular mass, denoted P, Q, R, S, and T, were prepared using a solvent gradient extraction technique at 160 °C with ethylene glycol monobutyl ether as solvent and diethylene glycol monobutyl ether as non-solvent [5]. Also listed in Table 1 are two pairs of fractions, A1, A2 and B1, B2, each differing in tacticity for essentially the same mass. These were prepared similarly but at 125 °C with xylene as solvent and ethylene glycol monoethyl ether as non-solvent. Size exclusion chromatography was used to measure the molecular masses and their polydispersity while the pentad sequences used for the values of isotacticity came from ^{13}C nuclear magnetic resonance spectroscopy.

Table 1
Molecular data for the homopolymer and fractions.

Material	$M_m \times 10^3$	M_m/M_n	%mmmm
Homopolymer	541	5.9	91.4
P	63.5	2.1	83.2
Q	207	1.5	93.6
R	341	2.0	93.6
S	491	2.4	94.4
T	818	2.4	93.0
A1	91	2.7	45.7
A2	92	1.9	86.4
B1	192	2.5	67.7
B2	199	2.6	88.5

The principal experimental results were obtained by transmission electron microscopy of carbon replicas of permanganically-etched samples. Linear nucleation was used to give lamellar arrays aligned in row structures and thereby greatly simplifying the acquisition of lamellar thickness data. Two methods were adopted to this end, the second introduced later for fractions in limited supply.

In both cases, samples were stressed close to their melting point, to generate the linear nuclei, immediately crystallized isothermally in a nitrogen atmosphere on a controlled Mettler FP52 hot stage for the chosen time then finally quenched in cold water. In the first method, two roughened, shaped poly(4-methyl pentene-1) sheets were placed either side of a polypropylene pellet and the whole mounted as a sandwich between two Kapton sheets. This assembly was positioned on a Koffler hot bench where the polypropylene just started to melt, manually compressed using a cork while one poly(4-methyl pentene-1) sheet was slowly and steadily pulled away from the other, then quickly transferred to the hot stage. The presence of row structures is readily confirmed by polarizing optical microscopy. In the second method, glass fibres were laid on a pellet sample and pressed into it, between glass slide and cover slip. After cooling, the ends of the fibres were gathered together with cellulose tape (for easy pulling), the sample was melted at 200 °C in a Mettler FP800 stage for 1 min then crystallized, under nitrogen, in the FP52 hot stage and held in position while the fibres were slowly and steadily pulled through. Row structures were produced in the wake of the fibres.

Prior to electron microscopy a suitable surface, produced if necessary by cutting the outer surface away at liquid nitrogen temperatures with a microtome, was etched. In this work the etchant was a 1% w/v solution of potassium permanganate in a 10:4:1 mixture of concentrated sulphuric acid, orthophosphoric

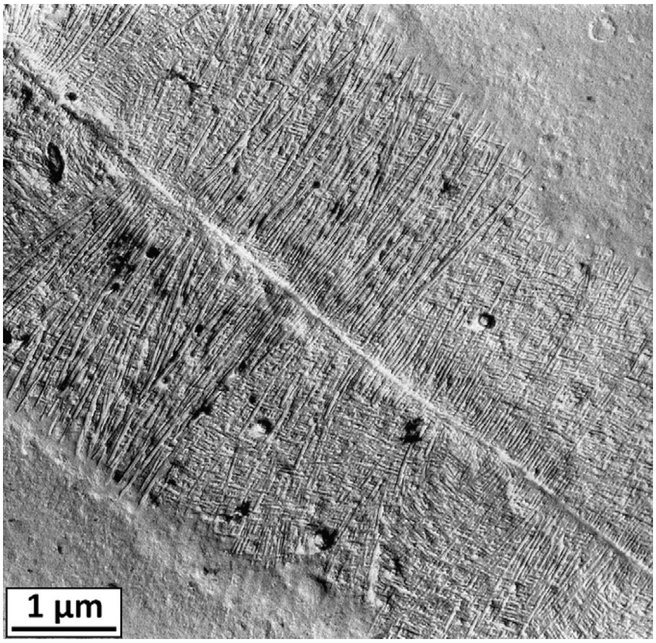

Fig. 1. A longitudinal section of a row of the homopolymer crystallized at 140 °C. In this perspective both radial and cross-hatching lamellae are oriented normal to the image, i.e. correctly presented for thickness measurement.