Polymer Vol. 37 No. 26, pp. 5933–5936, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00 + 0.00

S0032-3861(96)00626-X

On shish-kebab morphologies in crystalline polymers

A. W. Monks, H. M. White and D. C. Bassett*
J. J. Thomson Physical Laboratory, University of Reading, Reading RG6 6AF, UK
(Revised 23 May 1996)

Shish-kebabs or row structures consist of transverse lamellae growing from a central linear thread all with a common chain axis direction parallel to the central nucleus. Attention is drawn to the fact that adjacent lamellae are not in contact; in melt-crystallized α-polypropylene the separation is generally 3–4 nm. Moreover, lamellae in asymmetric environments, such as the ends of rows, are often elastically curved outwards. Both observations support proposals concerning the importance of cilia for melt-crystallized growth and the development of spherulites but would have been difficult to establish without the advantage of oriented nucleation. The former leads to values for the effective dimensions of cilia, the latter to values of the pressure they exert on an adjacent lamella. The advantages of using linear rather than point nuclei in evaluating melt-crystallized morphologies are emphasized. Copyright © 1996 Elsevier Science Ltd.

(Keywords: shish-kebabs; cilia; melt-crystallization)

The so-called shish-kebab or row-structure morphology is a familiar feature of polymers crystallized under strain[1] yet the implications of its habit do not seem to have provoked comment even though they bear upon an issue central to crystallization from the melt, namely the role of molecular cilia in causing spherulitic growth and the consequent inherent spatial variation of physical properties[2]. Not only do shish-kebabs habits strongly support the existence of cilia but they can also provide quantitative data on their effective size and weak rubbery modulus. The value of shish-kebabs in simplifying polymer morphology has also been neglected. The geometrical control of morphology imposed by a linear nucleus brings many advantages compared to the unrestricted growth emanating from the point nucleus of a spherulite. It is much more straightforward to compile data on lamellar thicknesses in row structures than in spherulites, for example, and the lamellar environment is more uniform, and more readily established and assessed. The finite interlamellar separation is one such property; another, also described below, has been used to demonstrate for the first time that, during melt crystallization, crystallographic continuity will, if necessary, be sacrificed to the need to fill space. In this note, which precedes several detailed papers, we highlight the hitherto neglected importance of shish-kebabs to the investigation of central issues in polymeric crystallization.

The principal features of shish-kebabs are illustrated in *Figure 1* for a short length of linear nucleus in the α form of isotactic polypropylene from which lamellae have grown transversely. This particular figure is of a direct carbon replica of a permanganically-etched external surface of a thin film of a commercial homopolymer (kindly supplied by Mr Tetsuo Tsuboi of Adeka Argus Chemical Company, Japan), after crystallization at 125°C for 15 min followed by quenching into water at 10°C. In this instance the etchant consisted of a 1% w/v solution of $KMnO_4$ dissolved in a 40/60 mixture of H_2SO_4/H_3PO_4 conc. acids. Etching was for 3 h at room temperature; other procedures were as published previously[3].

Note first that adjacent lamellae are generally parallel but not in contact being separated by a well-defined interval of a few nm. This is an inherent feature which is also found, though to larger dimensions of ~ 100 nm, in shish-kebabs grown from perturbed solutions[1]. Its presence implies that something external to lamellae fills the space. By using α polypropylene we can show that this is not an 'amorphous' surface layer because although the space is too thin for parallel lamellae to form, minute twinned or cross-hatching lamellae have developed between the principal or radial lamellae as in *Figure 1*. We may conclude, therefore, that the interlamellar material is inherently crystallizable. Nevertheless it does not diffuse away even when growth is slow, at low supercoolings, so that it must be attached to the neighbouring lamellae. Such properties point to the interlamellar material as comprising the uncrystallized portions of molecules already partly attached to the growing lamellae, which are conveniently referred to as cilia by analogy with the filamentary growths in cells.

Lamellar thickness, interlamellar separation and radial growth rate are three of several parameters which have been measured in an extensive investigation[4] on shish-kebabs of α polypropylene, both of homopolymer and of two sets of fractions, separated by molecular mass and by stereoregularity respectively, as functions of crystallization temperature, molecular length and stereoregularity. This is believed to be the first time it has been possible to acquire such representative electron microscopic data of the interior of an unaltered melt-crystallized polymer. These trends of behaviour are repeatable and consistent irrespective of whether the row nucleus was generated by elongating the melt or by pulling an interstitial fibre. Moreover, the growth rates and lamellar thicknesses are the same as measured for spherulites and for transcrystalline layers.

---

* To whom correspondence should be addressed

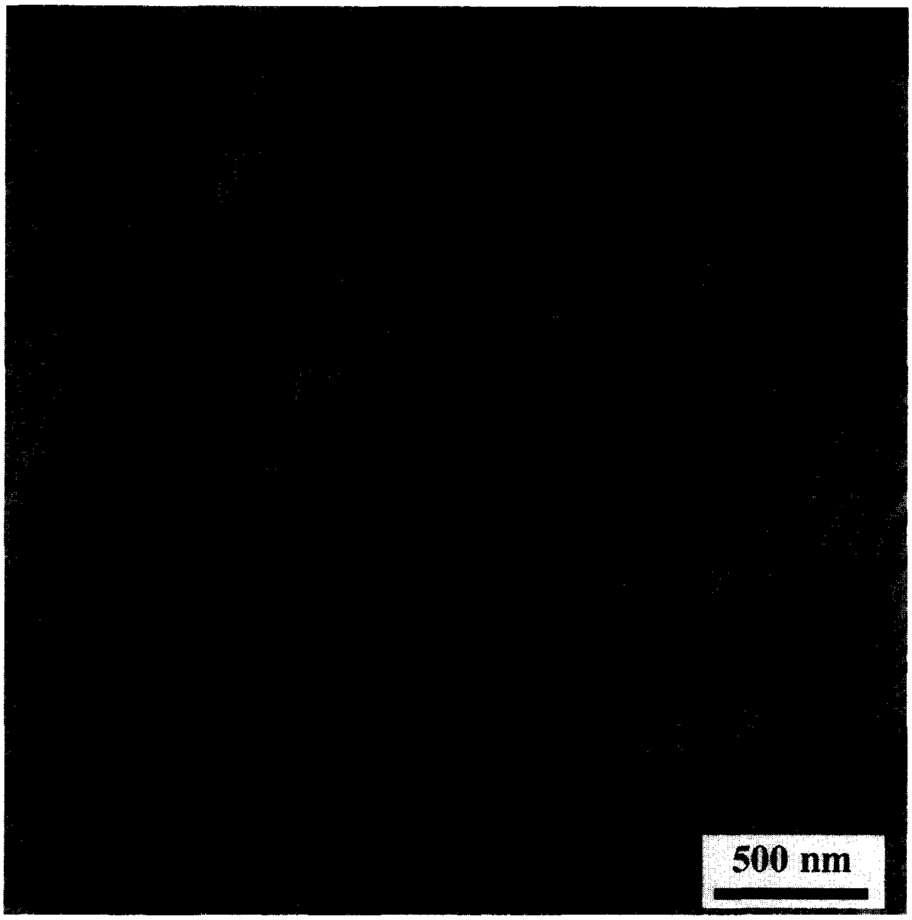

Figure 1 Longitudinal view of a row structure in α polypropylene grown at 125°C. Note the separation between adjacent lamellae and the elastically curved lamellae (arrowed) at the ends of the rows

We can be confident, therefore, both that the measured phenomena are of an innate growth feature and do not, for example, merely reflect an underlying periodicity in the nucleus greater than the lamellar thickness—the opposite of what would be expected in terms of the relevant supercoolings—and that they are pertinent to melt crystallization in general.

Cilia present between lamellae will exert a pressure equivalent, in general, to a weak rubbery modulus due to conformational distortion but rising at small interlamellar separations as bond distortion becomes a factor[2]. This pressure can be estimated from the curvature of lamellae such as those arrowed in *Figure 1* which are not infrequently observed in asymmetric locations within or at the end of shish-kebabs. The strain varies but does not exceed 1%, consistent with there being elastically bent (by adjacent cilia). The maximum curvature of such lamellae has been measured for α polypropylene across all the crystallization variables cited above leading to an *a priori* reasonable value for cilia pressure some two orders of magnitude less than the modulus of natural rubber.

These findings are of particular significance because cilia are believed to be responsible for spherulitic growth and the concomitant spatial variation of properties in polymers[2]. This suggestion was put forward when electron microscopy of representative microstructures showed that old ideas based on cellulation were untenable with the spherulitic skeleton being established by individual dominant lamellae rather than the groupings which had previously been assumed. In particular, the regular splaying apart of adjacent lamellae in sheaflike precursors[5,6], such as in *Figure 2*, pointed to the presence of a short-range repulsive force operating near the branch point. Further work demonstrated that it is an inherent feature of a melt-grown lamella that adjacent layers diverge from branch points, typically giant screw dislocations[7].

Most recently the role of cilia has been confirmed by work on the monodisperse long-chain paraffins following earlier work which revealed their quantised lamellar thicknesses[8–10]. Studies of pure n-$C_{294}H_{590}$ have shown that it does form spherulites from the melt but only when lamellae contain chainfolded molecules and not when molecules are fully extended[11,12]. This is in accord with a simple expectation, whereby cilia will be a (possibly transient) feature of chainfolded growth but not when molecules add in extended form. The demonstration that the nature and properties of cilia can be evaluated by the examination of shish-kebabs is, therefore, particularly apposite.

The second principal benefit of examining shish-kebabs is that their oriented growth allows the efficient acquisition of data that would not otherwise be readily accessible. This stems from their consistent crystallography and the ability to observe many lamellae with the same desired orientation. Longitudinal views as in *Figure 1*, i.e. with the length of the row and, therefore, the chain axis in the specimen plane, display the chain extension of lamellae whose traces are normal to the row,

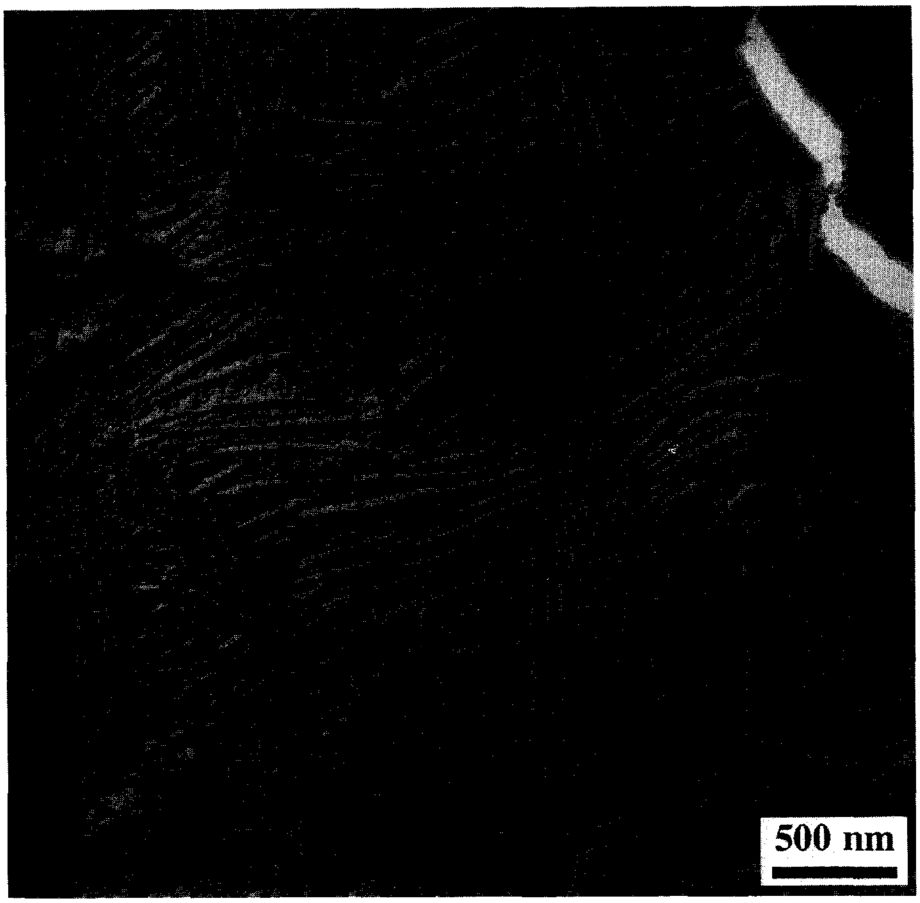

Figure 2 Sheaflike appearance of an immature spherulite of α polypropylene crystallized at 125°C. Note the separation and mutual divergence of adjacent lamellae

which for typical systems, in which chain axes coincide with lamellar normals, is also the thickness. This is correctly presented for measurement in shish-kebabs. By contrast, lamellae present in differing orientations in spherulites must be tilted (about their traces as axis) to ensure that the measured dimension is normal to the viewing direction. This not only is laborious but also measures a less-precisely-defined population than is characteristic of row structures. For them, all radial lamellae are equal and grow outwards in a parallel array and uniform environment. By contrast, in spherulites the first forming dominant lamellae create a diverging, branching framework within which later-forming lamellae develop, but these are necessarily more constrained during growth than were their predecessors, leading to differences in thickness and melting point within a more disperse total population[13].

Lamellae seen at other than perpendicular orientations to the row indicate that, for them, the chain axis is inclined to lamellar normals. This is generally true of polyethylene whose lamellar fold surfaces are $\{h0l\}$ for growth from quiescent melts, i.e. lamellar normals have been rotated around **b** away from the chain axis **c**; **b** is also the growth direction. One can measure the chain tilt directly by observing lamellae down **b** i.e. in the centre of an off-diametral plane of the row structure. This has been done in a recent study of crystallization under shear which has shown that chain inclination decreases (so that lamellar surfaces become more strained) as shear rate increases[14]. In this way it was demonstrated that, contrary to previous opinion, the lamellar component of a shish-kebab does not form under strain-free conditions.

For α polypropylene, cross-hatched and radial lamellae are mutually twinned with a common **b** axis; **a*** is the growth direction. A comparison of their respective thicknesses may be obtained in longitudinal views of the diametral plane of a row (for which **b** coincides with the direction of observation). Both lamellar thicknesses are then correctly presented for measurement while other statistics such as the frequency of cross-hatching and interlamellar separations may readily be obtained[4].

Transverse views of row structures, i.e. down the chain axis, present different opportunities. For example, a recent study of partly melted, then recrystallized, compacted polyethylene fibres has demonstrated that growth from separate nuclei around the fibre surface interacts to produce cooperatively twisted banding[15]. Although long suspected, this cooperativity had not been confirmed from studies of spherulites, because for them all growth could, in principle, be traced back to a single nucleus from which a common phase would follow.

Systematic study of transverse views of rows of α polypropylene, as functions of crystallization temperature, molecular length and stereoregularity, has also provided significant new information. In particular it has been shown that the long-standing premise of crystallographic continuity along the radius of a spherulite—indicated by the maintained sense of banding along a radius—can be overridden in order to fill space. It is possible to do this with α polypropylene because of its characteristic lathlike crystal habit. When laths grow out from the centre of a row, lateral gaps will develop between them with increasing radius. This space cannot be accessed by continuous radial or cross-hatched growth without deformation, such as twisting around the radius. In practice the gaps are filled in for all but the least stereoregular polymers. New growth is nucleated on the sides of the radial laths, with the plane of these lamellae approximately parallel to the axis of the row[2,4]. Clearly the opportunity of filling space has been taken notwithstanding the concomitant necessity of creating discontinuous crystallography. This secondary nucleation must, moreover, have been rapid in relation to the rate of crystallization in order for the row to maintain its cylindrical envelope.

In all of the above ways, especially in its evaluation of the nature and properties of cilia, the examination of shish-kebab or row structures is making significant contributions to our understanding of the molecular processes of polymeric crystallization. The intention of this note is to draw the attention of a wider audience to the considerable advantages of examining oriented rather than randomly distributed entities when evaluating the morphology of melt-crystallized polymers.

References

1 Bassett, D. C. 'Principles of Polymer Morphology', Cambridge University Press, 1981
2 Bassett, D. C. *Phil. Trans. R. Soc. Lond. A.* 1994, **348,** 29
3 Olley, R. H., Hodge, A. M. and Bassett, D. C. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17,** 627
4 White, H. M. Ph.D. Thesis, University of Reading, 1995
5 Bassett, D. C. and Olley, R. H. *Polymer* 1984, **25,** 935
6 Bassett, D. C. and Vaughan, A. S. *Polymer* 1985, **26,** 717
7 Bassett, D. C., Olley, R. H. and al Raheil, I. A. M. *Polymer* 1988, **29,** 1539
8 Paynter, O. I., Simmonds, D. J. and Whiting, M. C. I. *J. Chem. Soc., Chem. Commun.* 1982, 1165
9 Bidd, I., Holdup, D. W. and Whiting, M. C. *J. Chem Soc., Perkin Trans. 1,* 1987, 2455
10 Ungar, G., Stejny, J., Keller, A., Bidd, I. and Whiting, M. C. *Science* 1985, **229,** 386
11 Bassett, D. C., Olley, R. H., Sutton, S. J. and Vaughan, A. S. *Macromolecules* 1996, **29,** 1852
12 Bassett, D. C., Olley, R. H., Sutton, S. J. and Vaughan, A. S. *Polymer* 1996, **37,** 4993
13 Bassett, D. C. and Patel, D. *Polymer* 1994, **35,** 1855
14 Hosier, I. L., Bassett, D. C. and Moneva, I. T. *Polymer* 1995, **36,** 4197
15 Kabeel, M. A., Bassett, D. C., Olley, R. H., Hine, P. J. and Ward, I. M. *J. Mater. Sci.* 1995, **30,** 4694