A comparison of oligomers and polymers in poly(aryl ketone): effect of chain folding on crystal morphology and generalizations therefrom

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Single crystals were prepared from poly(phenyl ethyl ketone) (PEK) oligomers and compared with those of the corresponding polymer with respect to morphology, electron and X-ray diffraction patterns. The present comparison shows a drastic change in morphology when going from the extended chain oligomer to the folded chain polymer, the regular, lozenge-shaped crystals of the oligomer degenerating into irregular, knobbly laths for the polymer. At the same time the diffraction patterns are becoming more poorly defined, the reflections broadening and shifting to smaller angles (these effects being largest along the *a* direction) all indicating reduced lattice perfection. All these effects, the degeneration in the morphology and lattice order, must clearly be associated with chain folding in the polymer. The above is in sharp contrast with the behaviour of the paraffin–polyethylene system where the onset of chain folding with increasing chain length has no qualitatively noticeable effect on morphology and lattice order. We envisage the effects in PEK arising due to the more bulky and stiffer character of the chains which, while folding for kinetic reasons, cannot do so over a similarly short distance as in the paraffin–polyethylene system or other flexible polymers. The larger fold-spans then require larger volume along the fold surface exerting stresses on the underlying crystals. These stresses, being cumulative, will expand and distort the lattice and eventually set a limit to the size of the coherent structure entity in the growing crystal leading to the observed irregular, knobbly morphology. We venture to generalize this scheme to other members of main chain aromatic polymers, and beyond, to all regular polymers which crystallize slowly and with poorly defined morphologies with the difficulty in folding being the common factor.As a further step, we also invoke the degenerate morphologies of copolymers of otherwise fully flexible chains where exclusion of crystallographically incompatible comonomer units (e.g. branches) from the crystals would be expected to give rise to cumulative strain with analogous consequences.

(Keywords: PEK oligomers; crystal morphology; effect of folding)

INTRODUCTION

The message of the present paper is on two levels. The first is the specific recording of certain experimental facts accessible for the first time, and the second is the enunciation of some generalizations suggested by the specific observations of potential wider relevance to polymer crystallization: specifically why certain chemically regular chains give rise to poorly defined morphologies and yield correspondingly low degrees of crystallinity.

The factual basis of the work rests on the recent availability of oligomers of poly(phenyl ether ketone) (PEK), a member of the currently topical polyaryl family of which poly(phenyl ether ether ketone) (PEEK) has attained technological significance. We find that in the PEK system there is a distinct morphological transition when going from the chain extended oligomers to the chain folded polymer for an otherwise unaltered crystallography, accompanied by a significant deterioration in crystallinity (or crystal perfection). This behaviour is in sharp contrast to the previously explored n-alkane–polyethylene system where progression from the chain extended oligomer to the chain folded polymer leads to no basic difference in morphology and crystal perfection. The underlying experimental material, including a juxtaposition of the two behaviour types, will be presented.

The generalization indicated above takes its starting point from the fact that the PEK chain is much less flexible than the alkane–polyethylene chain. Its different behaviour when passing from extended to folded configuration will be attributed to the difficulty in folding of such less flexible chains which leads to certain specific consequences recognizable experimentally. Then, encouraged by the apparent fruitfulness of this approach we shall venture beyond the present experimental material extending our argument to other low crystallinity polymers including those with chain irregularities,

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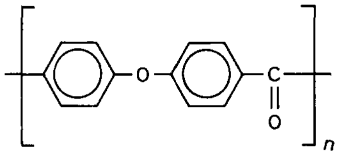
displaying features similar to those in the present PEK system.

EXPERIMENTAL

Materials and methods

PEK and its oligomers (synthesized at ICI) have been used throughout with the general formula:



Structurally each of the oligomers possessed phenyl groups at both ends. Where the material contained an even number of phenylene rings, the groups adjacent to the end rings were both ether linkages and hence the chains were symmetrical. Where the chains contained an odd number of aromatic groups the linkages next to the end rings comprised of one ether and one ketone group. The samples available were oligomers possessing 3, 5, 6, 7, 8 and 9 phenylene rings in total and in this paper the oligomer in question will be identified by the number of phenylene groups in the chain.

For the present purposes PEK is very similar to the more extensively studied PEEK[1–8]. Thus the morphology of solution grown crystals of PEK and PEEK, are almost identical[5,7]. In terms of chemical structure PEK has equal numbers of ether and carbonyl groups spaced alternately along the backbone on either side of the phenylene rings (*Figure 1*). In terms of crystal structure[3–5] it has identical orthorhombic crystal symmetry and virtually identical cell parameters to PEEK: $a = 7.76$ Å, $b = 6.00$ Å and $c = 10.0$ Å. Projections of both the (1 0 0) and (0 0 1) planes of the PEK unit cell are shown in *Figure 1*.

Electron microscopy coupled with electron diffraction was used for the study of single crystal morphology. Accordingly, the oligomers were crystallized from solution, in the present instance from 1,2-methyl pyrrolidinone for the longer and from acetone for the more soluble, shorter members. In most cases crystallization was induced by cooling below the dissolution temperature (which of course increased with oligomer length). Once crystallized, the specimens were prepared for transmission electron microscopy (TEM) by drying drops of the resulting suspensions onto carbon film supported by electron microscopy grids. In the case of the shortest oligomer, which was reluctant to crystallize, the acetone solution was dropped directly onto carbon-coated grids so that crystals grew on evaporation of the solvent. When dry, in some cases, the specimens were obliquely shadowed with platinum–palladium alloy. The PEK polymer was crystallized by cooling a hot benzophenone solution as described in reference 5.

X-ray diffraction was applied in two contexts. First, to identify the spacings and thus establish the crystallography in the PEK oligomers, particularly in relation to the PEK polymer, and second, to measure line widths and crystal dimensions deriving therefrom in the light of questions arising through the morphological studies. Flat plate photographic recording was used for the former and diffractometry for the latter with further details given below.

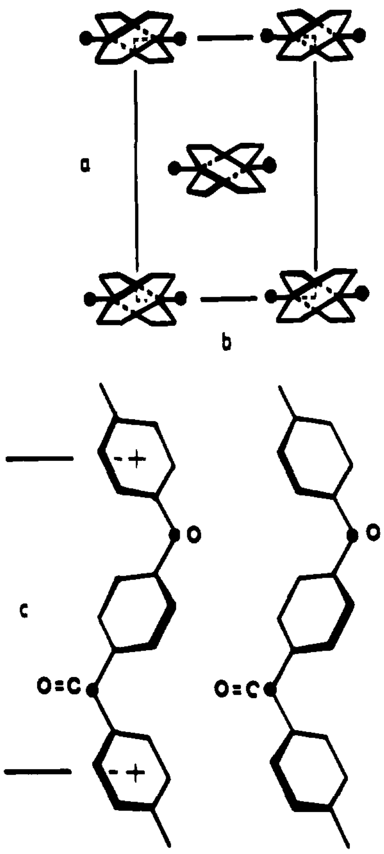


Figure 1 Crystal structure of PEK (after the isomorphous structure of PEEK[3]) in projections parallel (top) and perpendicular (bottom) to the chain direction

RESULTS

X-ray diffraction patterns of the oligomers (in the form as received) revealed that all reflections, except those at the lowest angles, were essentially identical to the reflections in the PEK polymer demonstrating that the packing of the chains in the crystals of the oligomers is identical to that of the corresponding polymer.

These diffraction effects are readily explained in terms of the crystal structure of the oligomers. X-ray structure determination of PEEK and PEK oligomers, using macroscopic single crystals[6] show that the mode of crystallization is analogous to that of paraffins relative to polyethylene. The oligomer chains pack together in layers with essentially identical conformations and packing as the chains in the crystal lamellae of the PEEK and PEK polymers. The layers in turn stack on top of one another so as to register the ends of the oligomer chains. Thus diffraction from the structure within the layers will produce reflections that correspond to the reflections from the polymer crystals. However, there will be additional diffraction from the full stacked cell of the oligomers, of which the most prominent will correspond to the stacking thickness which will be directly related to the length of the oligomer chain.

The above stacking thickness as determined from two orders of the corresponding reflections is listed for each oligomer in *Table 1*. *Table 1* also contains the calculated values of the extended chain lengths. Both are in the expected sequence and increase in the same proportion when proceeding from lower to higher oligomers, except that the spacings are slightly larger than the chain lengths

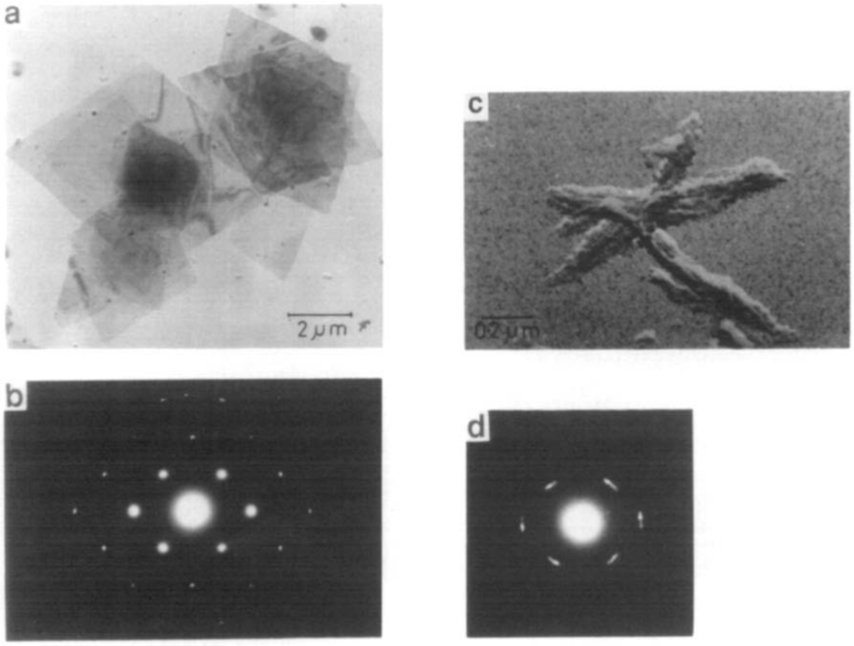


Figure 2 PEK morphology and diffraction. (a) Crystal of oligomer 7 (chain extended). Electron micrograph, unshadowed. (b) Electron diffraction of an oligomer crystal as in (a). (c) Crystal of PEK polymer (chain folded) at the extremity of a sheaf. Electron micrograph, shadowed. (d) Electron diffraction pattern of a PEK polymer as in (d)

Table 1 Oligomer long periods calculated from first and second order reflections and theoretical extended chain lengths

Oligomer	First order *d*-spacing (nm)	Second order *d*-spacing (nm)	Theoretical extended chain length (nm)
3	1.56 ± 0.02	–	1.4
5	2.60 ± 0.03	2.61 ± 0.03	2.4
6	3.36 ± 0.05	3.55 ± 0.04	2.9
7	3.77 ± 0.06	3.75 ± 0.03	3.4
8	4.29 ± 0.06	4.27 ± 0.04	3.9
9	5.07 ± 0.09	–	4.4

reflecting the fact that the spacings also accommodate the end-to-end separation.

By electron microscopic examination the crystalline oligomer precipitates were found to consist of well defined lozenges extending over several micrometres, an example of which is shown in *Figure 2a*. Clearly, there are great similarities between the oligomer crystals and those of polyethylene and the paraffins (see below).

A typical oligomer electron diffraction pattern is shown in *Figure 2b*. The reflections are all *h k* 0, again showing the crystal to be in the *c* axis projection. Also, again as in the case of the alkanes, *a* and *b* are parallel to the long and short diagonals of the lozenges, respectively, and the edges of the lamellae are {*h k* 0} faces.

When passing on to the polymeric version of PEK the morphology changes dramatically. The electron micrograph of *Figure 2c* shows the trend. As has been previously documented in detail, both by ourselves[5] and Lovinger and Davis[7,8], the crystal entities are only a few micrometres in size and essentially irregular and lath-shaped. The irregularity is manifest through jagged edges and overall knobbly appearance, the latter on the scale of ~20 nm. The knobbly lamellar entities nearly always display some rather irregularly disposed multilayering with single layered structures, where identifiable, confined to the extreme tips of the laths.

An electron diffraction pattern, taken with a small beam (~1 micrometres) from the lath tips, so as to minimize the randomizing effect of the multilayering, is shown in *Figure 2d*. In this case, since many crystals are slightly randomized about a common orientation, the reflections no longer appear as spots but as arcs. The strongest reflections are 1 1 0 and 2 0 0; some non-*h k* 0 reflections also appear but with very much reduced intensity[5]. The overall disposition of the *h k* 0 arcs corresponds to the *c* axis view of the PEK lattice just as for the single spots in the case of the oligomers (*Figure 2b*). Thus, in agreement with previous findings[5,7], the basic laths are single crystals seen essentially in *c* axis projection, where by the familiar argument, the polymer crystals must be chain folded. It follows that the drastic difference in morphology between oligomer (*Figure 2a*) and polymer (*Figure 2c*) is associated with the difference in molecular trajectory, namely, whether it corresponds to extended or folded chains, or vice versa, and that chain folding leads to a drastic deterioration in the morphological regularity.

Figure 3 shows the corresponding situation for the paraffin–polyethylene system. This is familiar material, to be invoked in the present juxtaposition with the new material in the discussion below.

The deterioration in crystal regularity in the PEK system, when going from oligomer to polymer, is paralleled by the definition of the reflections in the diffraction patterns. In order to assess this quantitatively, X-ray diffraction line profiles were recorded in the case of X-ray powder patterns comparing oligomer and polymer under otherwise identical circumstances.

Examples of X-ray diffractometer data from the higher angle region for PEK polymer and a typical oligomer are shown in *Figure 4*. These curves have been derived

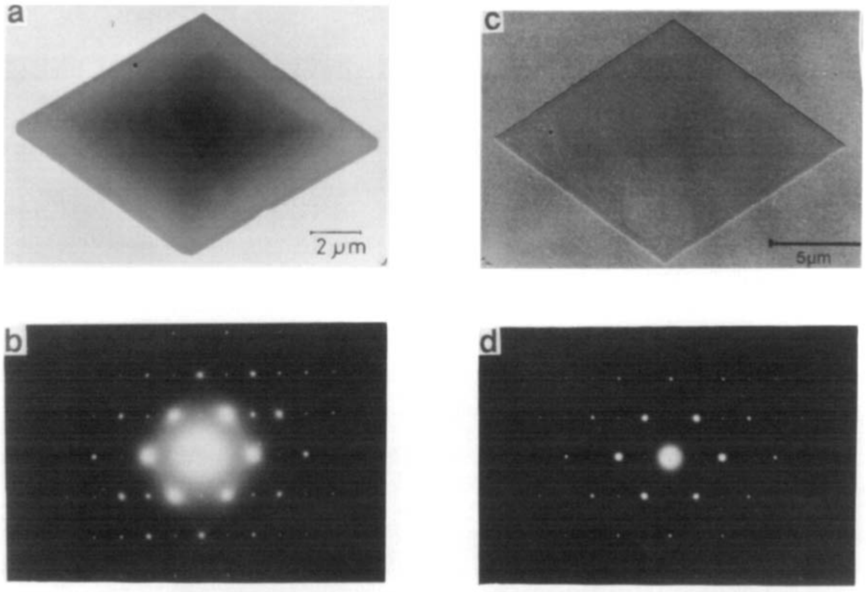


Figure 3 Paraffin–polyethylene morphology and diffraction. (a) Crystal of an n-alkane, $C_{36}H_{74}$ (chain extended). Electron micrograph. (b) Electron diffraction pattern of an n-alkane crystal as in (a). (c) Crystal of polyethylene (chain folded). Electron micrograph. (d) Electron diffraction pattern of the crystal in (c)

Table 2 Summary of X-ray diffractometry results. Spacings, line broadening (β) and apparent crystal size (L) for oligomer 7 and PEK polymer with two different thermal histories for (1 1 0) and (2 0 0) reflections

	Spacing (nm)			Line width (β^0)			Crystal size (L, nm)		
		PEK			PEK			PEK	
X-ray reflection	Oligomer 7	230°C	320°C	Oligomer 7	230°C	320°C	Oligomer 7	230°C	320°C
110	0.468	0.473	0.471	0.30	0.81	0.61	3.0	1.10	1.46
200	0.378	0.387	0.384	0.30	1.41	1.03	3.0	0.64	0.88

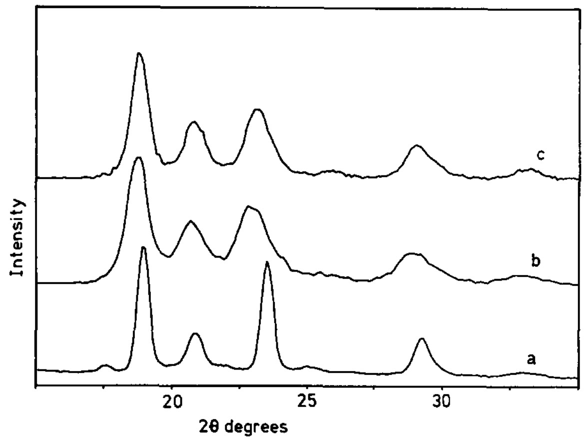


Figure 4 X-ray diffractometer traces of: (a) oligomer 7; (b) PEK polymer moulding crystallized at 230°C; (c) PEK polymer moulding crystallized at 320°C

from a Philips diffractometer used in the transmission mode with a slit configuration giving a machine broadening (based on a quartz standard) with a half-height width of 0.45°. Curve A shows the raw data from the seven-ring oligomer packed in a Lindenmann tube of 2 mm diameter (cf. 0.5 mm beam width). Curves B and C are derived from two 0.1 mm thick mouldings of PEK that had been isothermally crystallized at 230 and 320°C, respectively. The total scatter in the original PEK data had a large diffuse component from the non-crystalline regions. In order to make the data more easily comparable with the oligomer data, the non-crystalline contribution has been subtracted by fitting a scaled curve from a quenched amorphous sample of PEK.

The first three main peaks in the curves in *Figure 4*, correspond to the 1 1 0, 1 1 1 and 2 0 0 reflections of the PEK cell. In the PEK case the peaks are at noticeably lower angles than for the oligomer, and thus correspond to larger spacings. The spacing values for the 1 1 0 and 2 0 0 reflections are given in *Table 2* from which it will also be apparent that the relative spacing increase is largest for 2 0 0. Also in the PEK cases the peaks are broader than for the oligomer where the peak widths are only slightly wider than the machine broadening indicating a very small intrinsic width. An additional important feature to note is that for the PEK curves the 2 0 0 at around 23° is substantially broader than the 1 1 0 at around 19°. The half-width values (β) for 2 0 0 and 1 1 0, after making a correction for machine broadening, are given in *Table 2*. Unfortunately there is no 0 k 0 reflection with which to directly gauge the broadening along the b crystal direction. Even so, from the above comparison between 1 1 0 and 2 0 0, it is clear that there is significant broadening for the polymer compared to the oligomer and that this broadening is substantially greater along the a direction indicating that the PEK crystallite size is either smaller or the distortion there is larger in the a than in the b direction.

We may express the above line widths in terms of apparent crystal size (L) using the Scherrer equation:

$$L = \frac{K\lambda}{\beta \cos \theta}$$

by taking $K = 1$ and inserting corrected half-widths for β. The results for one oligomer (taking the seven-ring as an example) and for the polymer crystallized at two different temperatures are shown in *Table 2*.

We see that when going from oligomer to polymer the increase in spacing and decrease in crystal size, as reflected by line broadening, go hand in hand: the larger spacing corresponds to smaller (and possibly more distorted crystal) where both effects are largest along the a axis direction.

DISCUSSION

Clearly in the PEK system there is a distinct morphological transition between chain extended oligomers and the chain folded polymer despite the fact that both exhibit the same crystal structure. This is in contrast with the previously extensively explored n-alkane–polyethylene system which is here invoked for comparison through *Figure 3*. *Figure 3a* is an example of an extended chain paraffin and *Figure 3c* that of polyethylene with corresponding diffraction patterns (*Figures 3b* and *d*), which, as familiar, correspond to c axis views in both cases. We see that there is no qualitative difference between the extended chain n-alkane (oligomer) and chain folded polymer, both giving rise to regular lozenges and associated unarced purely single crystal diffraction patterns. (This juxtaposition of extended and chain folded crystals could be fine-tuned further by turning to the recently available strictly uniform ultralong n-alkanes where extended and folded chain lamellae can be obtained for one and the same compound by varying conditions of crystallization[9,10].)

The different behaviour of the PEK and n-alkane–polyethylene systems must undoubtedly reside in the folding ability of the two different chain types, where the PEK chain is expected to be less flexible than polyethylene.

In the case of polyethylene it is reasonably well established that the molecule does form, or at least is capable of forming, a tight fold. Furthermore, we may expect there to be a reasonable degree of re-entrant (or near re-entrant) folding resulting in a smooth fold surface.

However, in the case of the PEK system, the comparative chain inflexibility suggests that the molecules cannot fold back adjacently, but only over more than one, possibly several, stem repeat distances. Thus it is to be expected that the folds will not be adjacently re-entrant and that in all probability the fold surface will be irregular, and as a consequence to a large extent disordered. Further, the diminished ability of the chain to fold is expected to enhance multilayer formation. Namely, there should be a larger proportion of cilia which have not found appropriate refolding sites within the same layer at a given stage of crystallization. Such cilia could then form new nuclei on the surface of the parent layer leading to multilayers or could become built into an already growing layer at some distance from it. In either case, interlamellar tie molecules or large loops, will be constituents of disorder along the lamellar surface and/or interlayer structure.

The nature of fold surface and/or interlayer is of course a long standing and much debated subject in polymer science. It is recognized that there are limits to the disorder that can be created along crystal surfaces while retaining full molecular continuity with the crystal, or alternately, the disorder, such as may be present, must necessarily affect the molecular continuity, hence degree and type of folding, between the crystal and the disordered zone. Due to matching requirement of zones of lower and higher bulk densities along surfaces of fixed cross-sectional area all chains cannot pass from crystal to amorphous zone; some must either terminate or fold back, conditions definable in strict mathematical terms[11].

The issue here becomes particularly pertinent for the present case of PEK because of the fold surface–interlayer disorder which is anticipated as an intrinsic consequence of the restrictions on folding. We suggest that such restrictions, via the matching problem, would lead to a domain structure disrupting both the lattice and morphological continuity of the crystal layer. A domain structure in the form of knobbliness is in fact a prominent feature of PEEK–PEK crystals which have already prompted specific crystallographic suggestions by Lovinger and Davis regarding their origin[8]. In the position of the new, and we believe crucial, information that this knobbliness (and in fact the whole degeneration of the regularity of crystal habit) sets in with chain folding, when passing from oligomer to polymer, we can now propose a more general explanation incorporating amongst others also the Lovinger–Davis model. In fact, our proposal to be outlined is not confined to the present family of polymers but extends to all crystallizing polymer systems where the amorphous nature of the interlayer is intrinsic and unrelievable through alternate modes of threading chains through the system.

The argument is as follows. We have an amorphous zone along the crystal interface (in the case of PEK arising because of the large loops and numerous cilia consequent to restrictions on sharp folding behaviour). If the chain flux from crystal to amorphous zones is equal to the number of stems in the crystal, which will be the case with PEK if the large folds are counted as part of the amorphous region, this will cause (plain) biaxial surface stresses within the crystal. The strains required to relieve these stresses*, if homogeneously distributed, will be incompatible with the existence of a crystal lattice; hence such a crystal will simply not form.

However, it will be apparent that for a small cluster of stems the excess volume can be taken up by 'bulging out' of the chains at the edges with correspondingly lower surface stresses at the interface. Such stress relieving effect of the lateral crystal edge will, however, diminish rapidly as the crystal becomes larger laterally. In other words, for a specified interlayer structure the stress will build up cumulatively on lateral crystal growth. At a diameter

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* For amorphous and crystal densities of 1.272 and 1.430, respectively, this will amount to ~0.11 strain per end surface area of crystal at room temperature. In fact at the elevated temperatures of crystallization, where the systems come into being, ~300°C, the density differences, hence the resultant strain will be considerably larger

where the stress becomes prohibitive, further lateral growth should stop. In this way the existence of a low density surface layer, without the possibility of reducing chain flux from the high density crystal to the low density interlayer (as achievable by tight folding, e.g. in polyethylene), will limit the lateral crystal size. We suggest this as the origin of the observed knobbly morphology and degeneration of crystal regularity in a folded system.

The above is fully compatible with the scheme by Lovinger and Davis proposed to account for certain morphological features in PEEK single crystals[8], namely ready cleavage interrupting growth more readily normal to *b* than along it, thus giving rise to the observed faulted grainy structure of the layers and the preferred growth direction along *b* with the correspondingly elongated layer habit. Our scheme now provides the stresses to which the crystals would then respond in the way proposed by Lovinger and Davis. Further, we now know that this degeneration, both in layer perfection and habit, is the consequence of folding, hence the stresses responsible for it must originate from the fold surface. If in addition the stress field in the interlayer itself is anisotropic, due to a preferred fold direction, then this will compound with the anisotropy of lattice forces influencing the anisotropy in the resulting domain structure and crystal habit accordingly. This could e.g. accentuate the fragmentation along *b*†.

The above issue, namely that the maximum lateral crystal size is limited by cumulative stresses has already been addressed and treated by Hoffman[13,14] to account for the limited fibrillar crystal diameter arising on flow-induced crystallization. In spite of differences in terms of the molecular arrangement, the situation is formally identical to the one considered here: cumulative biaxial surface stresses at the crystal–amorphous interface affect and eventually stop lateral growth. For surface and lattice parameters appropriate to polyethylene, the domain sizes are found to be in the range of 10–30 nm. As far as these parameters are not altogether different for the PEK–PEEK system we would expect similar values also here. Indeed Lovinger and Davis quote 15–20 nm as the mean size of the nodules, values we here substantiate by our own observations.

There is one major difference, however. The theory[13,14] identifies the lateral dimension of an isolated crystal entity and indeed, the flow induced fibrils are such entities. The domains in our PEEK and PEK crystals, however, are contiguous, giving rise to coherent, even if rough and jagged lamellae with the same common orientation throughout. We have to hypothesize therefore that, having approached a maximum size, lateral growth does not stop at once along all directions (in which case only fully dispersed submicroscopic 'blobs' would result). Instead, statistically, growth would continue in some directions longer than along others, which would give the system a chance to renucleate growth at some places of the previously interrupted growth before the primary growth of the original domain stops all round. This would preserve physical coherence and overall orientational correlation between domains throughout a given layer while the cessation of primary domain growth would leave its mark in terms of a region of crystal imperfection. The latter in fact is a necessity if the cumulative surface strain is to be relieved (the factor stopping the growth in the first place), and it is this imperfection which makes itself morphologically apparent in the form of 'knobs'. Nevertheless, sufficient memory of the underlying perfect lattice may remain to induce nucleation of the new domain and transmit its orientation to it. In the specific case of our PEK, this would mean that primary growth continues along *b* longer than along *a* before becoming interrupted. This then would create domain boundaries when traversing the crystal along *a* with connecting crystal bridges along *b*, the latter ensuring continuity within the otherwise knobbly crystal.

Our X-ray line broadening measurements are fully supportive of the above considerations. In the first place they show that the crystals are smaller and/or less perfect in the polymer than in the oligomer and that this size/perfection reduction is significantly larger along *a* than along *b*. Interpreting the effect purely in terms of size the above means that we have domains elongated along *b* consistent with the overall morphological observation of the knobbliness and preferred growth direction pointed out by Lovinger and Davis previously[8]. The numerical values for the domains, derived on size basis alone (*Table 2*) are consistent with the scale of the knobbliness.

Recently further information through direct electron microscopic lattice resolution on PEEK crystals has become available[15,16]. This reveals the existence of discrete domains of lattice coherence over the crystal, amongst others, as seen in *c* projection, in other words that the lattice is not continuous over the full crystal area. The domains are visibly elongated along *b* with dimensions, as resulting from quantitative evaluation, being quoted as 10 nm along *a* and 25 nm along *b*. The numerical agreement between the dimensions of these electron microscopically observed coherent lattice domains and the value derived from our X-ray line broadening measurements can hardly be fortuitous. In fact, closer inspection of the micrographs in references 15 and 16 even suggest crystal bridges along *b*, all this in full qualitative and quantitative agreement with our results and suggested model.

The observed larger lattice spacing in the polymer, as compared to the oligomer, is also consistent with the lattice being strained, where according to our picture, the source of strain is the fold surface layer. The existence of such lattice strains, as manifest by enlarged spacings is in fact an integral part of Hoffman's model of cumulative strain invoked to account for the self limiting lateral size of fibrous polyethylene crystals[13,14]. In the present case of PEK, the anisotropy of the spacing increase (largest along *a*) should clearly have additional information to convey on the nature of the surface layer causing the strain, hence on the nature of the folds themselves*. This promising opening would require a

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† The fact that there is an interaction between the amorphous and crystal components, specifically that there must be stress exerted by the amorphous interlayer on the crystal lattice, has emerged recently from studies on the thermal expansion coefficient of PEEK along the different lattice directions[12]

* In the case of the polymer (PEEK, PEK) variations in lattice spacing with crystallization conditions and heat annealing have been reported before[17,18]. In particular, decrease of spacing was attributed to perfectioning of the crystal. However, the variations involved were small, typically between 0.77 nm and 0.78 nm for the *a* dimension; the present effect involving the oligomers is outside this range altogether (0.75 nm for *a*)

combined examination of line broadening and spacing shift, which, however, leads to beyond the scope of the present work.

Nodular layer structures with jagged edges and irregular habits are widespread amongst polymer single crystals. They are common features in aromatic polymers like poly(ethylene terephthalate) and polycarbonate[19,20]. Their origin here is likely to be the same as now proposed for PEK. This, if further substantiated, would shed new light on an old and controversial issue regarding the reality and origin of this knobbliness while bringing a welcome rational unification to widely disparate observations within the whole field.

We may even venture further and bring in the diverse observations on branched polyethylene and ethylene–propylene copolymers within the same conceptual umbrella. As known for considerable time, such polyethylenes give small, irregular, jagged edged and highly 'knobbly' crystals when grown from solution[21–23] in sharp contrast to the crystrallographically well defined fully linear polyethylene (e.g. *Figure 2c*). Here the chains are flexible in both the linear and branched version and thus both could fold sharply. But now it is the lattice which does not accept all the branches with consequent increase of amorphous material at the layer interface. The latter then would generate unrelievable surface stresses which then would lead to a domain structure in the way proposed for PEK. We propose, therefore, that knobbly layer structures and irregular habits arise beyond a certain degree of disorder along the layer surface, which in turn can arise when chains are intrinsically incapable of folding sharply, or when substantial portions of imperfect chains become unacceptable to the lattice, which then reacts back on the folding behaviour accordingly.

To end with, it needs stating that the concept of domains is of course not new. Under the name of mosaics, balls or nodules, etc., they have been frequently invoked before in polymer crystals (as in fact in all crystals) as a direct observational fact, or as derived from other properties (e.g. X-ray diffraction line broadening). We maintain that here we have made a new contribution to this long standing, often diffuse and debated topic by relating it through direct experimental observation to the onset of chain folding in polymers in cases of chains which do not fold and/or crystallize readily. This whole issue should be assessed and pursued further, say by measuring lattice strain and comparing the behaviour of chains with systematically varied chemical constitution.

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