High-Temperature Crystallization and Morphology of Poly(aryl ether ether ketone)

Andrew J. Lovinger,* Steven D. Hudson, and Don D. Davis

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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ABSTRACT: We have investigated the structure and morphology of the high-performance polymer poly(aryl ether ether ketone) (PEEK) crystallized at temperatures between 300 and 320 °C. We found no support for suggested changes in crystal structure, growth face, growth direction, or gross spherulitic morphology. In addition to narrow, fibrous lamellae, we provide evidence for large, branch-like, composite lamellar stacks and for primary growth of lamellae in the form of bundles. We have discovered a second morphological form of PEEK in thin films grown at high temperatures. This consists of large (order of μm), faceted single crystals in a flat-on orientation (i.e., parallel to the substrate), having the same unit cell and *b*-axis preferred-growth direction as the usual fibrous PEEK lamellae. However, in contrast to the latter, their molecular chains are not parallel to the lamellar normal but inclined to it by 38.1° about the *b*-axis, leading to {102}-type fold surfaces. Moreover, overgrowths of the usual fibrous PEEK lamellae are obtained in an edge-on orientation on the larger flat-on crystals. We show that both populations share the same *b*-axis growth direction and that the edge-on lamellae arise by quasi-epitaxial nucleation of their molecules along the [201] direction on the planes of their flat-on counterparts.

Introduction

Among the newer technologically important polymers, poly(aryl ether ether ketone) or PEEK is attracting increasing interest. This is based upon its high-temperature and high-strength properties, as well as its suitability for use in high-precision molded objects or composites.[1] Because PEEK is a semicrystalline polymer, we have been interested in its structure, crystallization, and morphology, as well as their effects on properties.

A number of authors have reported on the chain conformation and packing of PEEK.[2-7] The molecules adopt a planar-zigzag conformation defined by their ether and carbonyl groups (which are generally considered to behave isomorphously with respect to chain packing). The phenyl rings are tilted away from the zigzag plane by 37–40° in an alternating manner along the chains.[6,7] The unit cell is orthorhombic with $a = 0.783$ nm, $b = 0.594$ nm, and $c = 0.986$ nm,[6] all of which contract slightly during heating.[7]

As regards its morphology, PEEK crystallizes in the form of spherulites,[8] which were first studied in detail by electron microscopy in thin films crystallized from the melt or from the glassy amorphous phase.[9] We found these spherulites to consist of unusually narrow lamellae growing along their *b*-axes and nucleated preferentially in contact with the substrate;[9] this is caused by favored deposition of the *bc* plane onto substrates and leads to an edge-on orientation of the lamellae. Using a permanganic etchant, Bassett and co-workers[10,11] explored the internal microstructure of bulk PEEK, confirming the existence of narrow, lath-like lamellae and dividing these into two populations of (a) primary lamellae growing freely into the melt and (b) subsidiary lamellae growing in a restricted fashion between the dominant ones.[11] This dichotomy was also invoked to explain the unusual doubly-endothermic melting behavior of PEEK,[11-13] which has been documented by detailed thermal studies.[11-16]

To explore the morphology of *individual* lamellae under controlled conditions, we crystallized PEEK from two different solvents and obtained the first single crystals of this polymer[17,18] As in the case of melt-grown PEEK, the solution-grown spherulitic lamellae and individual crystals were fibrous, growing preferentially along the *b* crystallographic axis and cleaving along the (200) planes.[18] At higher crystallization temperatures, broader and less anisometric spherulitic branches and single crystals were observed.[18] Similar results were later obtained by Waddon et al.[19] and Tsuji and co-workers[20,21] (the latter having also resolved lattice images of PEEK).

However, despite all this work, a number of major fundamental questions persist regarding the structure, morphology, and crystallization of PEEK, especially at high temperatures. Some of these are motivated by its doubly melting behavior. The possibility of a second form differing in growth-axis orientation has been raised.[22] Even though the unit cell may be preserved, differences in growth face can lead to major morphological and thermal changes, as documented, e.g., in polyamides[23,24] and in *cis*-polyisoprene.[25] An intriguing proposal of a second morphological form at high crystallization temperatures has recently been made by Marand and Prasad[26,27] on the basis of optical micrographs of PEEK spherulites grown at $T \geq 295$ °C. Other related questions also need to be considered, e.g., the existence or absence of lamellar stacks vs individual dominant lamellae[11] or possible interfacial-tension effects as a source of biaxial orientation in thin films of PEEK.[22] In this report, we have attempted to address these various issues and to obtain a better understanding of the high-temperature structure, crystallization, and morphology of PEEK.

Experimental Section

The polymer used was obtained from ICI Ltd. in the form of unfilled, free-flowing granules and was the same material employed in our previous studies.[9,17,18] Its molecular weight is not known, but PEEK samples from the same manufacturer have been found to have $\bar{M}_w$ of 38 600[16] or 40 000[11] and $\bar{M}_n$ of 14 000[16] or 22 400.[14] Our samples had a melting point of 344 °C and a glass-transition temperature of 145 °C, both recorded at 10 °C/min. To study their morphology at high crystallization temperatures, we prepared thin films by casting from benzophenone at temperatures close to its boiling point onto freshly cleaved mica plates. The films were held in the melt at 380 °C for 10 min under flowing dry nitrogen and subsequently crystallized isothermally at the desired temperatures (above 300 °C). Following growth for specified periods of time they were rapidly cooled to ambient temperature to quench the remaining polymer to the amorphous state. After oblique shadowing with Pt/C and coating

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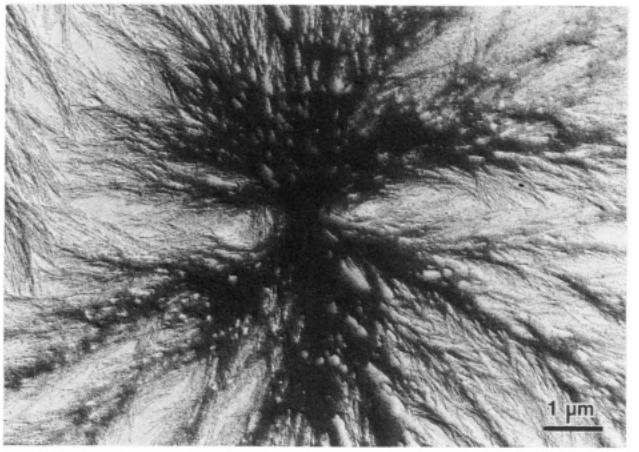

Figure 1. Morphology of a PEEK spherulite crystallized at 310 °C for 18 h, as seen in bright-field transmission electron microscopy.

with amorphous carbon in a vacuum evaporator, they were floated off their mica substrates onto water and examined by bright-field techniques and selected-area diffraction at 100 keV in a JEOL 100-CX transmission electron microscope.

Results and Discussion

For temperatures of crystallization up to 300 °C, the morphology of PEEK is as described previously,[9] i.e., spherulites consisting of narrow, lath-like lamellae, which in thin films adopt an edge-on orientation (this leads effectively to cylindrical symmetry of the spherulites about the *a*-axis). The typical appearance of our PEEK samples crystallized at higher temperatures, specifically 310 °C, is seen in Figure 1. They consist of spherulites which are remarkable in that their central portions are much more electron-dense than their peripheries. However, as seen in this figure, the darker regions also continue outward along some branches, occasionally extending all the way to the spherulitic periphery. These results are consistent with the optical microscopic observations of Marand and Prasad.[26,27] Moreover, such darker regions are also seen (but more sparingly) at lower temperatures, e.g., 300 °C (see Figures 3 and 5 of our previous publication[9]). The regions that appear dark do so *not* because of diffraction contrast (there are no strong reflections in this orientation) but as a result of *thickness* contrast.

From the distribution and shape of the (white) shadows within these thick, dark regions it is seen that the high-temperature lamellae are arranged in bundles with well-demarcated radial, and occasionally tangential, edges (the latter are more clearly visible toward the bottom of Figure 1). These features are seen more distinctly at the higher magnification of Figure 2a, which depicts a set of these thick, dark branches together with thinner regions interspersed in between. Our findings of two lamellar populations at high crystallization temperatures (consisting of (a) broad lamellar bundles yielding an overall branch-like morphology and (b) narrow, fibrous, individual crystals yielding a splay morphology) are in agreement with our previous results from *solution*-crystallized PEEK.[18] There, two similar types of morphology were seen when spherulites were crystallized in benzophenone at 220 °C, while only fibrous lamellae were grown at $T \leq 210$ °C (see Figures 3 and 1 of ref 18). Even though the temperatures where the two types of lamellae are observed are different in the cases of solution vs melt crystallization, the *supercoolings* are very similar. These findings also appear consistent with the conclusions by Bassett et al.[11] of primary, dominant lamellae growing in the open melt vs subsidiary, thinner lamellae growing in a constrained fashion between

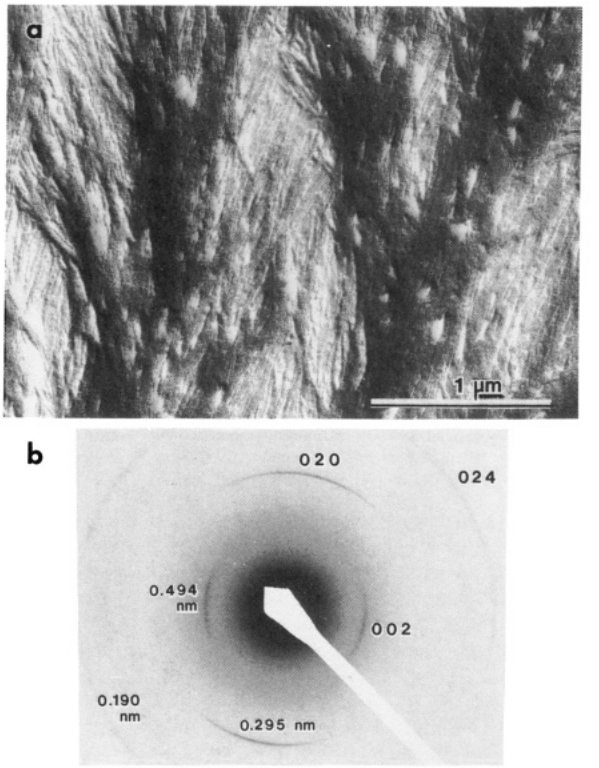

Figure 2. (a) Higher magnification of a region near the spherulitic periphery of Figure 1, showing the thick, dark branches as well as the thinner interspersed areas in almost parallel orientations. (b) Selected-area electron-diffraction pattern from the field in (a).

the former. Our electron microscopic findings may also apply to refs 26 and 27. The regions in our samples that contain lamellae in the optical microscope is the same as described by Marand and Prasad.[26,27] The lamellae within a bundle are stacked parallel and the bundles themselves are generally parallel to one another. The increased optical birefringence at high crystallization temperature is therefore consistent with the greater thickness and more perfect ordering of these broader lamellae. In contrast is the less birefringent lower-temperature morphology where splaying of individual, narrow lamellae is profuse.

We now examine the morphology of these thicker branches in greater detail by concentrating on regions at the periphery vs regions at the spherulitic centers (it has been shown by polarizing microscopy that these more birefringent regions occur much more frequently near the nucleus[26,27]). The field chosen for Figure 2a consists of an almost parallel orientation of the broad, dominant lamellae at the spherulitic periphery and therefore allows us to probe their crystallographic structure and unit-cell orientation. This is done with the aid of the selected-area electron-diffraction pattern of Figure 2b (correctly aligned to the field and arising overwhelmingly from the thicker regions), which shows all reflections to be of the 0*kl* type. The measured interplanar spacings in this figure are in agreement with those found at all lower temperatures and confirm therefore that polymorphism is *not* the origin of the morphological differences between the two populations.[26,27] Moreover, the relative dispositions of the observed 020 and 002 reflections demonstrate that this new, high-temperature morphological population has (a) the same *b*-axis preferred growth direction and (b) the same edge-on orientation in thin films as we found previously for crystals grown at all lower temperatures.[9] This latter conclusion is further reinforced by the total absence in Figure 2b of the 110 and 200 reflections, which are by far the strongest reflections in PEEK. That such

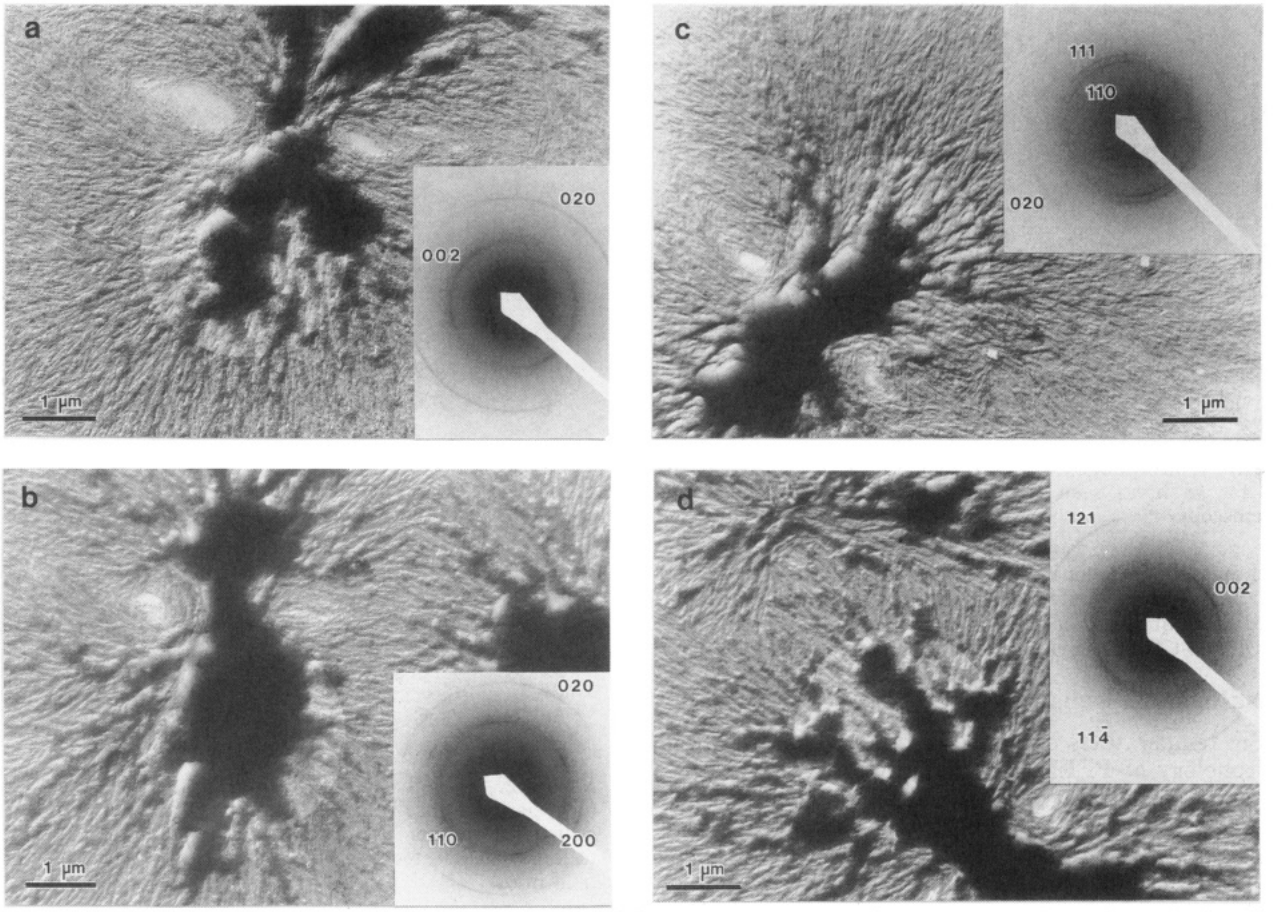

Figure 3. Typical bright-field electron microscopic images and diffraction patterns from regions near the nucleus of spherulites crystallized at 310 °C for 18 h. The diffraction patterns arise from the lighter circular areas delineated in each bright-field image by the selector aperture and imply an edge-on orientation in (a), a flat-on orientation in (b), and intermediate ones in (c) and (d).

an edge-on orientation is preserved even for the very tall, broad, high-temperature lamellar stacks (whose heights we estimate from shadow lengths to extend up to 130 nm) is remarkable. This does not appear to lend support to the suggestion[22] that the origin of the preferred edge-on growth is a biaxial orientation in the molten films arising from interfacial tension—especially in view of the relatively low molecular weights of these samples (whose fully extended length would be only 200 nm) and of their long residence times in the melt. The observed *b*-axis radial orientation also does not offer support to the possibility[22] that a change in growth face (as, e.g., in *cis*-polyisoprene[25] or even–even nylons[24]) might be responsible for the new morphology.

As far as thicker regions in the vicinity of the spherulitic nucleus are concerned, typical morphologies are seen in Figure 3a–d. The large, irregular, dark patches are entirely consistent with the optical microscopic findings.[26,27] Despite their obvious morphological differences from the more fibrous lamellae seen in these micrographs they have the *same* crystallography and growth direction, as deduced from the accompanying electron-diffraction patterns. While this is what we found also at the spherulitic periphery, there are differences in orientation. Specifically, the fields in Figures 3a and 3b represent the two extremes, namely an edge-on and a flat-on orientation, respectively. It is remarkable that this major morphological difference is not at all discernible from their bright-field images but only from their selected-area diffraction patterns (which show 0*kl* and *hk*0 reflections, respectively). An intermediate situation is depicted in Figure 3c, where the appearance and disposition of the 110 and 111 peaks imply that the broad lamellae are inclined about their *b*-axis growth direction by an average of 52° from their usual edge-on orientation. Finally, Figure 3d shows a case where the lamellae are growing out of the plane of the film (the diffraction pattern indicates an inclination of the *b* growth axis by about 27°). We therefore conclude that near the spherulitic nucleus extremely similar morphologies may arise from widely different and diverse assemblies of lamellae in these thicker regions. Here, in contrast to the thicker regions near the spherulitic periphery, the broader lamellar stacks are not necessarily on edge but may have a variety of orientations; in all cases, however, we find no evidence indicating polymorphism or change in growth direction or growth face.

It is, however, possible that structural differences might exist at higher temperatures, and efforts have in fact been made to correlate the two morphological forms with the two types of melting endotherm obtained in PEEK.[26,27] For this reason, we examined electron-diffraction patterns from PEEK at temperatures between ambient and the melting point. Four representative diffraction patterns from this temperature range are seen in Figure 4. The selected-area fields giving rise to these diffraction patterns were chosen from the region of the spherulitic center so as to contain predominantly contributions from the thick, dark branches (such as those shown in Figure 3a–d)). For specimens crystallized at 310 °C (such as those used for Figure 4), the lower and higher melting endotherms from DSC studies[11,12] peak at 315–320 and 340–344 °C, respectively. The diffraction pattern of Figure 4c is recorded at the lower DSC peak, while that in Figure 4d was obtained just before the final melting of the specimen (and well within the upper melting endotherm). The evidence from Figure 4 is clear; there is no polymorphic transformation or any other crystallographic change (with the exception of course, of thermal expansion of the lattice) at any tem-

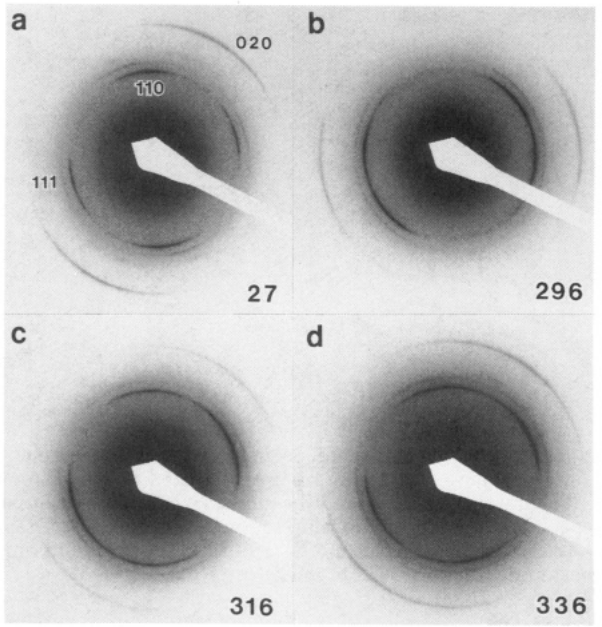

Figure 4. Electron-diffraction patterns recorded during heating at the indicated temperatures (in °C) from selected areas near the centers of spherulites that had been crystallized at 310 °C for 18 h.

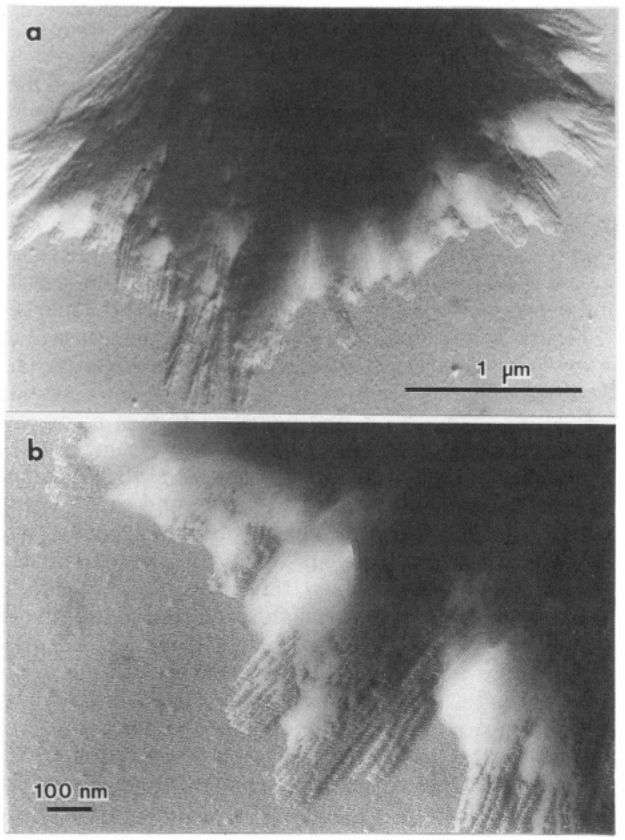

Figure 5. (a) Typical morphology of PEEK spherulites crystallized at 320 °C for 18 h, recorded by bright-field transmission electron microscopy. (b) Detail of growth tips from the spherulite in (a), showing crystallization of narrow crystals arranged in *bundles*.

perature up to the highest melting point.

Having discussed the typical morphology obtained at 310 °C, we now examine specimens crystallized at even higher temperatures. Growth at 320 °C yields spherulites that are exceptionally compact, dense, and uniform, as seen in Figure 5a. They differ from those obtained at 310 °C in that the dark areas are now much more compact and extend uniformly throughout the entire spherulite.

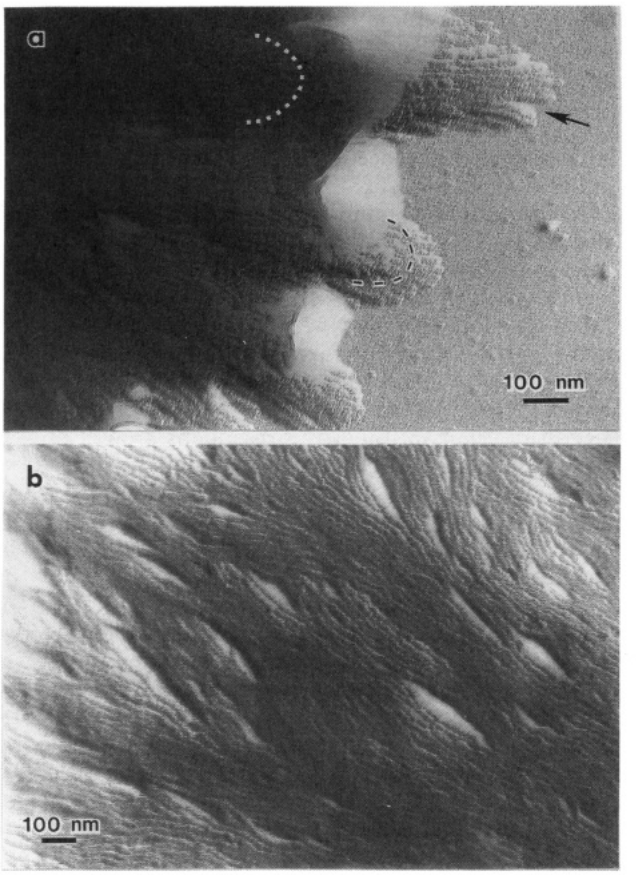

Figure 6. Electron microscopic evidence for growth in the form of lamellar bundles throughout the bulk PEEK spherulites crystallized at 320 °C for 18 h. (a) Overlapped tips of lamellar bundles seen *behind* the spherulitic perimeter; two are highlighted with dashed lines, while additional ones are seen toward the bottom. (b) Lamellar stacks in the *interior* of a spherulite, seen to be separated by radially oriented interbundle gaps. The spherulite grew from the lower right to the upper left corner.

Moreover, their thicknesses (i.e., the widths of their lamellar stacks) are also greater (up to 210 nm, based upon shadow-length measurements). An additional feature of major significance at this high crystallization temperature is seen upon examination of the growth tips (recorded at higher magnification in Figure 5b). The spherulitic tips are clearly observed to consist not of *individual* lamellae but of lamellar *bundles* growing together as stacks ca. 100–200 nm wide. This differs from the accepted understanding of PEEK spherulites as constructed from a framework of *individual* primary lamellae with subsequent infilling,[11] which is supported by our results at *lower* crystallization temperatures. At this highest growth temperature, even though infilling of constrained crystals must subsequently take place (leading to the observed lower DSC endotherm), the primary lamellae appear to grow *together* in clearly resolved stacks. These stacks would be much stiffer than individual lamellae, thus inhibiting splay and promoting parallel packing of stacks. This growth mechanism results in greater birefringence when observed via polarized optical microscopy.

A major concern about this conclusion is the possibility that these observed bundles might be only artifacts arising from surface tension and melt depletion at the very edges of the spherulite. However, they are in fact representative of the entire bulk of our spherulites as seen with the aid of Figure 6. Part a of this figure demonstrates that even *behind* the spherulitic growth front the fibrous crystals are organized together in the form of bundles that terminate in curved tips. Although rare in comparison to lower crystallization temperatures, lamellar splaying (ar-

rowed in this figure) is still the dominant mechanism for space-filling of PEEK spherulites (no screw dislocations have been seen in our samples or in published electron micrographs from other researchers). We therefore believe that at these very high temperatures the primary crystallization in PEEK occurs in the form of lamellar stacks, ca 100–200 nm wide, exhibiting irregularly curved fronts. Even in areas far behind the spherulitic periphery, this mechanism of stacked growth can be inferred from the bundle-like arrangement of individual lamellae, as seen in Figure 6b. The widths of the stacks discernible in this figure correlate favorably with the corresponding widths of the growth tips in Figures 5 and 6a. Moreover, the areas of that spherulite closer to its center (i.e., at the lower right of Figure 6b) exhibit fewer interstack gaps, suggesting their infilling by subsequent growth of subsidiary lamellae.[11] On the basis of the gap widths evident in this figure, these subsidiary lamellae would indeed be growing in a very constrained environment, which could then account for their lower melting point as suggested by Bassett et al.[11]

In our films, the lamellae crystallized at 320 °C have the same orientation to the substrate as at the lower crystallization temperatures, namely, edge-on. This was confirmed by selected-area electron diffraction, which yielded patterns identical to those obtained at lower temperatures, e.g., Figure 2b (such patterns are not shown here for the sake of brevity). Therefore, even at 320 °C and even in areas greater than 200 nm thick, the lamellae (while crystallizing in bundles) have their *bc* planes preferentially parallel to the substrate and grow along *b*. On the basis of this, we can obtain a direct estimate of lamellar thicknesses from edge-on morphologies such as in Figures 5 and 6. Indeed, from a set of 105 crystals we measured a periodicity of 14.4 ± 1.3 nm/lamella. This is in close agreement with long periods reported by small-angle X-ray scattering, i.e., those of Cebe[14] (15.4 nm at T_c = 319 °C) and of Lee et al.[16] (15.7 nm at T_c = 320 °C).

Having examined the spherulitic morphologies of PEEK at high crystallization temperatures (310 and 320 °C), we now turn our attention to single crystals of this polymer, which we have been able to obtain from the *melt* in thin films. This is important, because single-crystal growth has been examined up to now only from solution.[17–20] As we showed in the first reports of solution-crystallized PEEK,[17,18] single crystals consist of highly elongated narrow lamellae with *b* corresponding to the long axis of the crystal and *a* oriented transversely; the molecules were found to fold perpendicularly to the lamellar surfaces. These crystals showed extensive microfragmentation along *b*, as well as profuse disorder, yielding arced *hk*0 reflections. While their aspect ratio decreased with increasing growth temperature, order never improved beyond microfaceting, and reflections remained arced. These results were also substantiated in later studies.[19,20] For melt-crystallized PEEK, lamellae have almost always been seen in edge-on orientation. Where flat-on growth has been observed (namely within the "eyes" of some spherulites adjacent to their nuclei),[9] the protruding lamellar edges were very small, highly overlapped, and greatly microfaceted.

We have been able to induce a flat-on orientation in very thin areas by crystallizing at higher temperatures, as shown in Figure 7. A number of remarkable characteristics are exhibited by these crystals. First of all, they differ greatly from those obtained from solution in that they are not acicular and microfragmented but are instead large, fairly isometric single plates with well-developed faceting. They are slightly elongated along the *b*-unit-cell axis (see diffraction evidence later in this section), so that the 200 and 020 facets are prominently visible in Figure 7. Another important and unusual feature of these crystals is that they are accompanied by *profuse edge-on overgrowths* (these are numbered 1–3 in Figure 7). Moreover, these overgrowths are clearly aligned along the *b*-axis of the substrate crystal (overgrowth 1 in Figure 7 is initiated this way but curves away as the lamellae grow beyond the flat-on crystal). This very unusual mutual arrangement of flat-on and edge-on crystals is not accidental and may imply occurrence of a form of homoepitaxy, as we explore later in this report. A similar phenomenon is well documented for α-phase isotactic polypropylene.[28–30]

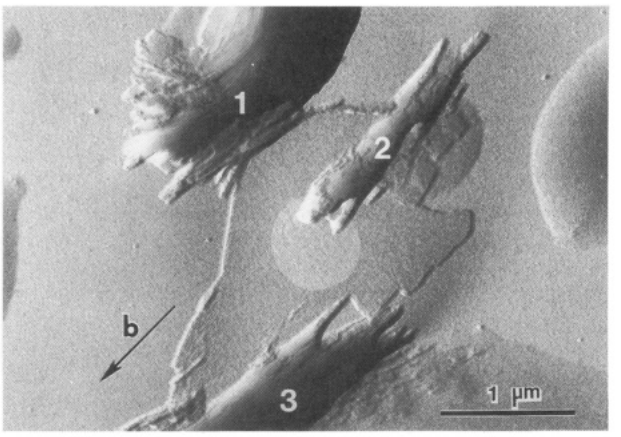

Figure 7. Morphology of single crystals of PEEK obtained in a flat-on orientation in thin films crystallized at 310 °C for 18 h. The numbered areas identify edge-on overgrowths that bear a specific molecular relationship to the flat-on crystal (see text). The circular region in the middle delineates the area from which electron diffraction was obtained.

To elucidate the origins of all these unusual characteristics of PEEK single crystals, we examined them by electron diffraction. A typical selected-area pattern is shown in Figure 8b, originating from the flat-on crystal and overgrowths of Figure 8a. (The circular area marked in Figure 7 yielded an exactly analogous pattern which, however, was too weak to be printed; similar patterns were obtained from other such crystals as well.) The diffraction pattern of Figure 8b is distinguished first of all by the *sharpness* of its reflections. This is totally uncharacteristic of all previously obtained patterns from PEEK single crystals (whose reflections were arced and diffuse) and points to the unprecedented regularity obtained here (consistent also with their morphological regularity discussed above). The sharp reflection at 0.296 nm is identified as 020 and confirms the preferred *b*-axis growth of the flat crystals. Moreover, this reflection is superimposed by a weaker *arc* with the same orientation. This arc is accompanied by another one at 0.497 nm, orthogonally disposed in Figure 8b and thus identified as 002. Both of these arise from the edge-on overgrowths, which are therefore seen to share the same *b*-axis growth as the flat-on crystal (again in agreement with the morphological evidence). In fact, regions of initiation of edge-on growth along *b* at the periphery of the substrate PEEK lamella are clearly visible (arrowheads in Figure 8a). Before we attempt to understand the reasons for this particular overgrowth formation, we need to identify the molecular arrangements in the flat-on crystals.

The major reflections are identified in Figure 8b by their interplanar spacings and shown schematically in Figure 9 in terms of their *hkl* indices. The patterns from all such crystals are complicated by the fact that the reflections present do *not* all belong to the same zone. We first attempted to interpret them on the basis of the major observed 110 and 020 reflections and of the expectation of a [001] zone; this is, of course, the general case for

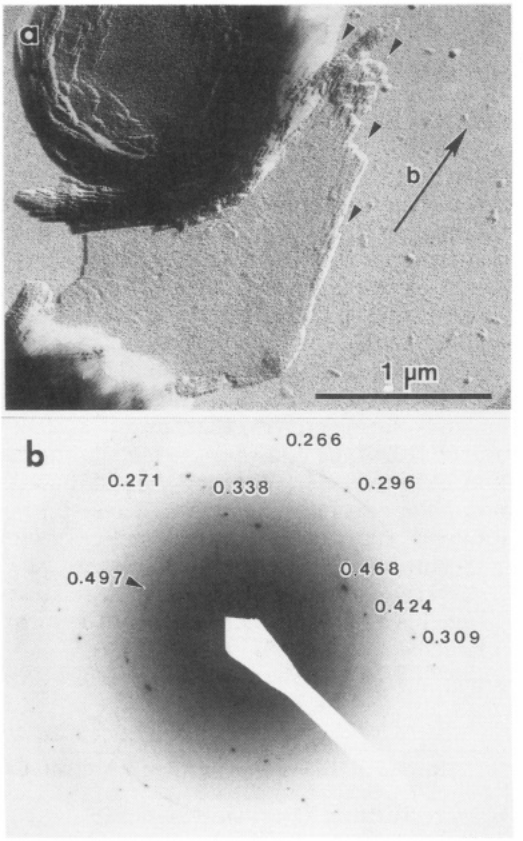

Figure 8. (a) Bright-field electron micrograph of a flat-on single crystal of PEEK and edge overgrowths crystallized at 310 °C for 18 h. Areas of initiation of edge-on growth along the *b*-axis are marked with arrowheads. (b) Electron-diffraction pattern from the crystal in (a).

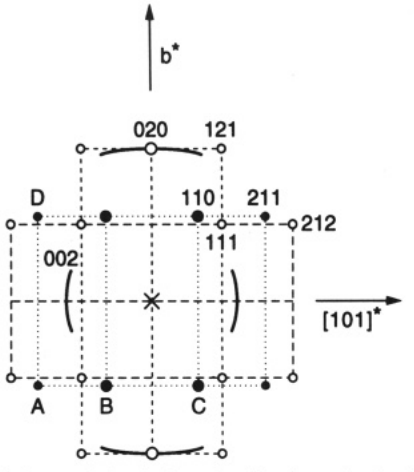

Figure 9. Schematic depiction of reflections obtained from flat-on crystals (circles) with edge-on overgrowths (arcs) during electron diffraction with the beam normal to the flat lamella.

polymers, where the chains are perpendicular to the lamellae, and has been found applicable to solution-grown PEEK single crystals[17,18] as well. However, this attempt was fruitless because the 110 peaks do *not* in fact belong to the reflecting plane. As seen in Figure 9, the reciprocal distance along b^* between the 110 spots (i.e., length DA) is not one-half of d_{020} but slightly larger. A similar effect is seen for the strong 211 reflections, which—contrary to their appearance in Figure 9—do *not* form a reciprocal lattice net with the 110 since distances BC and AB in this figure do not have any integral or rational relationship.

The *true* reciprocal-lattice net in Figure 9 is actually defined by the weaker reflections depicted by *open* circles, i.e., the 111, 212, 020, and 121. The reflecting planes are

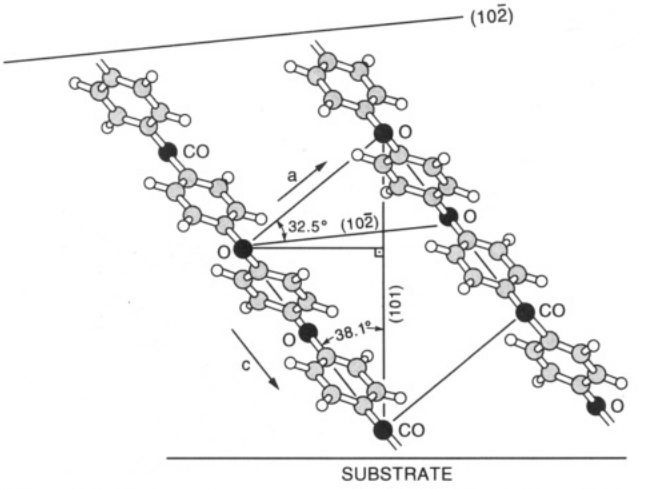

Figure 10. Schematic arrangement of molecules in the flat-on crystals of PEEK (such as in Figure 6), seen in *b*-axis projection.

thus of the (*hkh*) type and the electron beam is parallel to the [10$\bar{1}$] zone. This implies that the molecular stems are inclined about the *b*-axis by 38.1° from the lamellar normal in the manner depicted schematically in Figure 10. (For consistency with our earlier papers, angles are reported using the unit-cell dimensions of ref 3, which differ very slightly from those of more recent publications.[6,7]) The reason that the 110 and 211 spots are so prominently observed even though they do not belong to the (*hkh*) family is twofold: (a) the (110) and (211) planes are only slightly inclined to the [10$\bar{1}$] zone axis (by 21.9° and 14.2°, respectively), and (b) because of their strength and of the very thin lamellar habit, their intensity distribution in reciprocal space is in the form of a spike that intersects the sphere of reflection.[31]

The 38.1° inclination of the molecular stems to the lamellar normal is unusual but not unprecedented. In *solution*-grown crystals oblique stems have been extensively documented (e.g., for polyethylene,[32] poly(ethylene terephthalate),[33] and nylon 66[34]). For *melt*-grown polyethylene crystals, a 34.5° inclination is pervasive, leading to {201} fold surfaces;[35] this is attributed to better accommodation of folds at the crowded lamellar surfaces. An even higher inclination (44°, corresponding to {301} folds) was found in polyethylene single crystals grown *flat-on* on mica[36,37] (i.e., in the same manner as our PEEK single crystals). In the γ-phase of poly(vinylidene fluoride) a 28.5° inclination has been documented in detail.[38] Reasons for the 38.1° chain tilt observed in our PEEK lamellae are expected to be similar to those for the other polymers, i.e., fold crowding and preferential interactions with the substrate. As seen in Figure 10, an *exact* 38.1° chain tilt would not lead to any reasonable (low-index) fold surface, in contrast to the well-known case of polyethylene. However, it is likely that the crystal surface is (10$\bar{2}$), which deviates by only 5.6° from exact orthogonality (see again Figure 10).

{102} fold planes coupled with the observed molecular inclination also lead to a possible explanation for the growth of the *edge-on* lamellae on top of these flat-on crystals, as shown in Figure 7. It will be recalled from this figure that the *b*-axes of both edge-on and flat-on lamellae coincide (at least in the region of initiation). Moreover, the distance between chains in the [201] direction (which represents the intersection of the (10$\bar{2}$) and *ac* planes) is only slightly smaller (by ca. 7%) than the *c*-axis repeat. This would make it possible for PEEK chains to align themselves quasi-epitaxially in the [201] direction on the *ac* growth surfaces of flat-on lamellae, as depicted schematically in Figure 11. (This schematic is not meant to

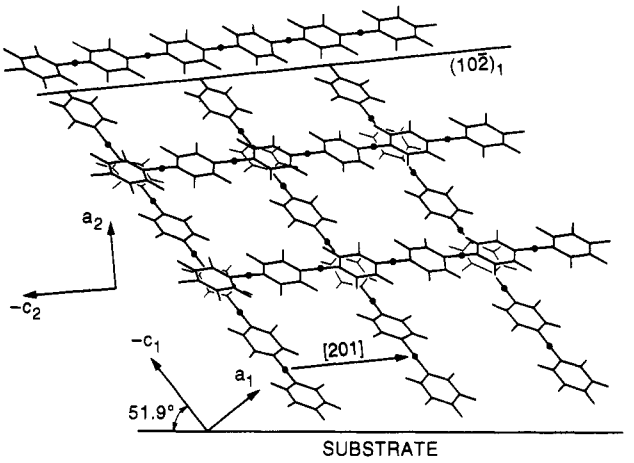

Figure 11. Model of quasi-epitaxial nucleation of molecular chains of PEEK along the [201] direction on *ac* surfaces of flat-on crystals, seen in *b*-axis projection. Subscript 1 refers to the lattice of the flat-on lamellae, while subscript 2 corresponds to that of the edge-on crystals resulting from this quasi-epitaxial molecular arrangement.

imply a unique possibility: the chains could be placed along [201] in mirror orientation with respect to the *ac* plane, the phenyl rings could be staggered rather than overlapped, etc.) In all cases, the PEEK chains deposited along [201] of the flat-on lamella would naturally cause growth of *edge-on* crystals having their *a*-axes close to normal to the substrate. Such edge-on lamellae would, of course, be taller than their flat counterpart, so that they will eventually grow *on top* of it (i.e., backward along *b*), as well *ahead* of it (i.e., forward along *b*). Both of these growth manifestations are observed in the bundle of edge-on lamellae numbered 2 in Figure 7. Thus, despite possible initial impressions from Figure 7, the edge-on crystals are not nucleated on the top of the flat lamella (which would be most unlikely because of its amorphous surface) but at its growth front. Instances where such incipient nucleation is observed prominently at the growth front are marked with arrowheads in Figure 8a; there they are also seen to block further growth of the flat-on crystal. In most cases, however, initiation of edge-on growth is not as frequent, which we attribute to the fact that the quasi-epitaxial match between the two orientations is not extremely close (ca. 7% difference). Interaction with the substrate appears to play a significant role as well, since the epitaxy is not usually reciprocated; i.e., nucleation of a flat-on crystal onto a preexisting edge-on crystal does not appear to occur commonly. In the case of isotactic polypropylene (α-phase), where the lengths of the *a*- and *c*-axes differ by only 2.3% and where interdigitation of the methyl groups is favored in both orientations, homoepitaxy of molecules along the *a*-axis is extremely frequent and well understood (see, e.g., refs 28–30).

Conclusions

In our electron microscopic investigation of PEEK films crystallized at high temperatures, we found no evidence to support suggestions of a different polymorphic form, change in preferred growth direction, or habit. We showed that the same kinds of spherulitic lamellae growing along *b* (and in an edge-on orientation in thin films) that have been described previously for crystallization at lower temperatures are also the dominant mode of growth for $T_c >$ 300 °C. However, as crystallization temperature increases, these lamellae become increasingly broader (taller in thin films) and grow together in the form of bundles which are densely packed together. This leads to an increased birefringence consistent with the optical findings of Marand and Prasad.[26,27] Near the spherulitic nucleus, a variety of lamellar inclinations (from edge-on to flat-on) is obtained.

In addition to the typical PEEK morphology of narrow, fibrous-like lamellae, we have discovered here a new one, occurring in very thin areas of our specimens at high growth temperatures (310 °C). This new morphology consists of large (order of μm), flat-on single crystals that are not distinctly anisometric but grow preferentially along their *b* crystallographic axis. We showed through electron-diffraction evidence that the molecular chains are tilted in these crystals by 38.1° about *b* such that the lamellar normal is $[10\bar{1}]$ and the broad amorphous surface is very close to $(10\bar{2})$. Because of the thinness of these crystals and the consequent electron-diffraction effects of their reciprocal lattice spikes, it is also quite possible (and in fact more likely during growth) that the fold surfaces are exactly of the {102} type and that the lamellar normal is thus 5.6° away from $[10\bar{1}]$. We found that this new tilted-chain morphology leads to growth of edge-on crystals adjacent to and on top of the flat-on lamellae. Actually, initiation occurs at the sides (*ac* facets) where we demonstrated a very reasonable quasi-epitaxial relationship for PEEK chains depositing along [201] of the substrate (flat-on) lamella.

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