Registry No. PAAA$_n$ (n = 1), 99328-04-8; PAAA$_n$ (n = 2), 99328-03-7; PAAA$_n$ (n = 4), 99328-05-9; PAAA$_n$ (n = 5), 99328-06-0; MAAA$_n$ (n = 1), 99328-11-7; MAAA$_n$ (n = 2), 99328-12-8.

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(21) The poly(amido amines) look like small molecules for which the precise site of protonation and "sharp" basicity constants can be determined. Because of the similarity with some branches of "classical" inorganic chemistry, their studies are known as "macroinorganics".

Solution Crystallization of Poly(ether ether ketone)

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ABSTRACT: The morphology of spherulites and single crystals of poly(ether ether ketone) (PEEK) obtained from two organic solvents (α-chloronaphthalene and benzophenone) has been studied by electron microscopy and diffraction. Spherulites were found to consist of very narrow, elongated lamellar branches that grow with the b crystallographic axis in the radial direction. Single crystals possess a spearlike habit, with b parallel to the long axis, a transverse, and c (i.e., the molecular axis) normal to the lamellar plane. This habit becomes less anisometric with increasing growth temperature. Both single crystals and lamellae exhibit significant disorder and fragmentation, consisting of microcrystals whose widths (~15–22 nm) are only slightly larger than their thicknesses (~12–15 nm). Flow-induced crystallization on a planar substrate has also been studied and found to yield a morphology of fibrous-lamellar composites with preferential orientation of the b axis parallel (and of the a axis perpendicular) to the substrate. The morphological features of PEEK crystals grown quiescently or during flow have been interpreted in terms of molecular structure and chain packing.

Introduction

Poly(ether ether ketone) (PEEK) is the most common member of a new class of high-performance engineering thermoplastics, the poly(aryl ether ketones).[1] PEEK, whose repeat formula is $-[C_6H_4OC_6H_4OC_6H_4CO]_n-$ (with all linkages at the para position), has a melting temperature of ~335 °C and a glass-transition temperature of ~145 °C. Because of its high-temperature/high-strength characteristics and melt processability, PEEK is generating much interest for applications such as reinforced composites,[2,3] coatings, electrical connectors, impeller housings, and many others.[2]

Molded specimens of PEEK have been examined by optical microscopy, differential scanning calorimetry, and X-ray techniques.[4] X-ray diffraction on uniaxially oriented samples[5,6] showed the unit cell to be orthorhombic (a = 7.75 Å, b = 5.89 Å, c = 9.88 Å) and very similar to those of other linear aromatic polymers, such as poly(p-phenylene oxide) [PPO][7] and poly(p-phenylene sulfide) [PPS].[8] More recently, a tripling of the c axis length has been proposed[9] to account for the chemical nature of the molecular repeat, although the chain conformation and packing have not been altered. X-ray diffraction and thermal techniques have also been used to study the effects of irradiation on molded PEEK sheets.[10]

One characteristic of PEEK that is of major importance in terms of performance, processability, and structural characterization is its exceptional chemical resistance.[2] PEEK is described as insoluble in all common solvents[2] with the exception of strong acids (e.g., 98% sulfuric acid,[1] hydrofluoric acid,[11] or polyphosphoric acid[12]); solubilization in these acids is effected by protonation. Of these, 98% H_2SO_4 has been most widely used for molecular weight determinations by viscometric[1,13] and light-scattering[13] techniques. However, the latter study[13] has shown that H_2SO_4 imparts significant chemical changes to PEEK as a result of extensive sulfonation. Therefore, strong acids are not appropriate for investigations of solution crystallization and morphology of PEEK, nor are they suitable for solution-processing techniques (e.g., casting or spin coating). Among other possible solvents mentioned in the literature,[1] the most effective have been found among the diaryl sulfones, although only at temperatures approaching the melting point of PEEK[1] (i.e., ~335 °C).

We have recently succeeded in dissolving PEEK in an organic solvent (α-chloronaphthalene) at much lower temperatures (~230 °C).[14] From this solvent, ultrathin films were cast that could then be melted and recrystallized from either the molten or the quenched glassy phases. Their resulting structure and morphology, as revealed by electron microscopy and diffraction, have been reported elsewhere.[15] Moreover, PEEK has also been crystallized from α-chloronaphthalene solutions in the form of single crystals,[16] immature and mature spherulites, as well as flow-induced fibrous lamellar aggregates. Recently, we have extended our solution-crystallization studies to a

Table I
Solvent Boiling Points (T_b) and Estimated Dissolution (T_d) and Crystallization Temperatures (T_c) Based upon Optical Clearing and Cloud Points of 0.1% Solutions of PEEK

solvent	T_b, °C	T_d, °C	T_c, °C
α-chloronaphthalene	263	228	213
benzophenone	305	245	225

second solvent, benzophenone, that allows growth of PEEK to somewhat higher temperatures than does α-chloronaphthalene. Preliminary findings on the single crystals grown from these two solvents have been reported in a short communication.[16] In this article we describe our results from a fuller structural and morphological investigation of single crystals and spherulites obtained from these solvents, as well as of aggregates produced by flow-induced crystallization in thin films.

Experimental Section

PEEK was obtained from ICI Ltd. in the form of unfilled, free-flowing granules. The molecular weight is not known, but a recent study by Bishop and co-workers,[13] using a range of developmental grades from the same manufacturer, found $\bar{M}_w \simeq 20\,000$–$35\,000$. The solvents used were α-chloronaphthalene (reagent grade from Fischer Scientific) with $T_b \simeq 263$ °C and benzophenone (99% pure, from Aldrich) with $T_m \simeq 48$ °C and $T_b \simeq 305$ °C. The polymer was dissolved in these solvents to concentrations of 0.01–0.001% by weight for single-crystal growth and 0.1% by weight for flow-induced crystallization.

After crystallization at the desired temperatures, the suspensions were cooled to room temperature and a drop from each was deposited on freshly cleaved mica for evaporation of the solvent in a vacuum oven. The crystals obtained were obliquely shadowed with Pt/C in a vacuum evaporator and then coated with carbon. The resulting thin films were floated off in water and picked up on copper screening, from which areas of interest (as revealed by optical phase-contrast microscopy) were then punched out in the form of 3-mm grids. These were examined by transmission electron microscopy and diffraction at 100 keV.

Results and Discussion

Estimates of crystallization and dissolution temperatures of PEEK in α-chloronaphthalene and benzophenone have been obtained from optical cloud points of 0.1% solutions cooled from ~250 °C at rates of 1–2 °C/min and subsequent clearing points upon reheating at the same rates. These estimates are given in Table I. From these, it is seen that both solvents have similar, fairly narrow intervals between dissolution and crystallization temperatures. As a result, benzophenone is the preferred solvent because α-chloronaphthalene is already very volatile at the temperatures required for dissolution of PEEK and because this solvent is well-known to discolor at those temperatures. We observed in both solvents that even above the dissolution temperature (where the solutions had become totally clear) a small number of particles was still insoluble; these remained so even at the boiling temperatures of the two solutions. PEEK, as manufactured industrially is known to contain a small amount of a "gel fraction", and we attribute to this (i.e., to cross-linked molecules) the insoluble particles seen. Moreover, even in the most dilute solutions, we consistently obtained not only single crystals but also axialitic and spherulitic aggregates. This suggests solution inhomogeneities, which may be related to the presence of some long molecules, cross-linked to different degrees. We describe below the three morphological types obtained in our studies, i.e., spherulites (including axialitic precursors), single crystals, and aggregates from flow-induced crystallization.

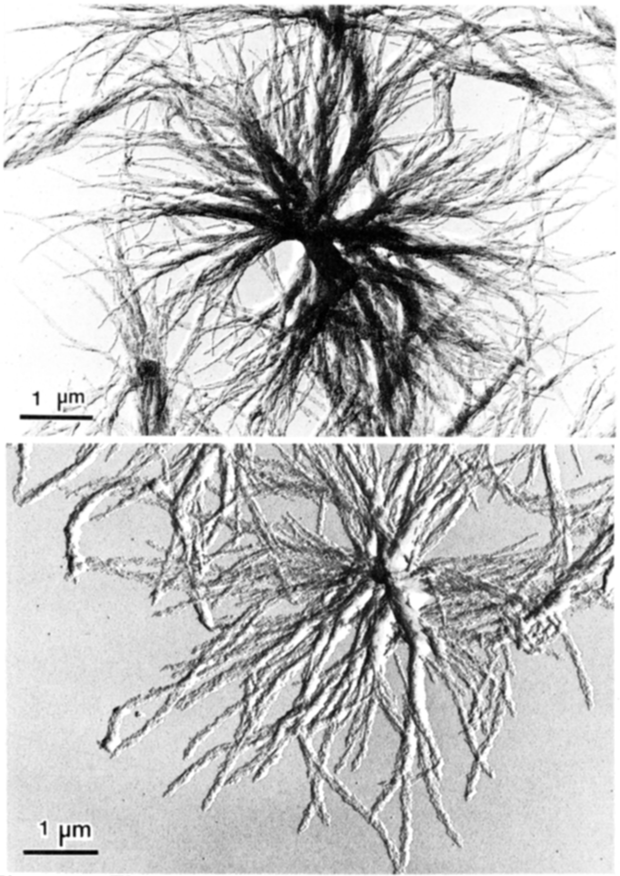

Figure 1. Electron-microscopic appearance of spherulites of PEEK crystallized from (a) a 0.01% solution in benzophenone at 210 °C, and (b) a 0.01% solution in α-chloronaphthalene at 205 °C.

Spherulites. The typical appearance of PEEK spherulites crystallized from benzophenone and α-chloronaphthalene at all temperatures below ~215 °C is seen in Figure 1. The homogeneously nucleated spherulite of Figure 1a shows the expected sheaflike growth, while its heterogeneously nucleated counterpart in Figure 1b exhibits radially directed growth from its center. The most significant and unusual characteristic of these spherulites lies in their long, yet narrow and spindly branches. These are seen in both parts a and b to extend over many micrometers in length but to be no wider than ~0.2 μm. Spherulites consisting of such narrow, fibrous crystals are not common among polymers, where broad, sheetlike lamellae are the rule[17] (notable exceptions include some polyamides,[18] barium polyglutamate,[19] and poly(*p*-phenylene sulfide)[20]). The radial growth direction of these PEEK spherulites corresponds to the *b* crystallographic axis (actual electron-diffraction patterns are shown in subsequent figures). We have found similar long and narrow lamellae growing in the *b* direction during our earlier study of PEEK crystallized from the *melt*; similar morphologies have also recently been revealed by permanganic etching of PEEK.[21] Such commonality of features from both melt and solution crystallization suggests that the unusually narrow lamellar habit is an inherent characteristic of this polymer.

In fact, closer examination of solution-grown PEEK spherulites at higher magnifications reveals that the lamellae of Figure 1 are actually composites of even finer microcrystalline subunits. These are clearly visible in Figure 2, which depicts the growth tips of one spherulite crystallized in benzophenone. The widths of these subunits are seen to range from 15 to 22 nm, which is only slightly larger than their thicknesses (12–15 nm at this crystallization temperature). These morphological sub-

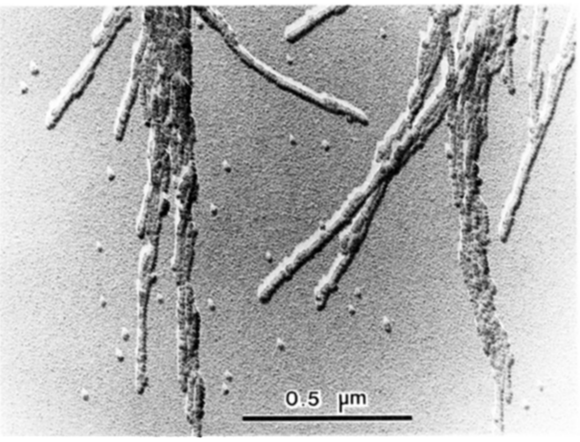

Figure 2. Detail of growth tips of a PEEK spherulite crystallized at 210 °C from a 0.01% solution in benzophenone.

units of PEEK are therefore highly exceptional among polymers in that they are not lamellar but truly fibrillar since they possess an essentially isometric cross-section. While fibrillar features of this type have also been found previously in ultrathin films of melt-crystallized PEEK, their true widths were partly masked by the small film thicknesses and the unusual edge-on crystalline orientation;[15] in the solution-crystallized spherulites, no such uncertainties prevail. Possible reasons for this exceptional narrow habit are discussed after description of single-crystal morphology in PEEK. We should also note from Figures 1 and 2 that the radial continuity of the fibrous subunits is also poor (with obvious "knobbed" and "mottled" features), so that even longitudinally the individual microcrystallites appear to be of very small dimensions.

When the crystallization temperature is raised, the spherulites grow with large arms that appear considerably broader than the lamellae described so far. This may be seen for crystallization from benzophenone in Figure 3a: thick and wide lamellar aggregates grown slowly at the selected crystallization temperature of 220 °C cover most of the field of view, while much narrower ones, apparently grown while the solution was being cooled to room temperature, are seen at the right. A higher-magnification view of the growth tips that are outlined at the top left of Figure 3a is shown in Figure 3b. Here, it is clear that the spherulitic arms are multilayered aggregates of crystals that exhibit definite signs of disorder, i.e., finely mottled morphologies and absence of macroscopic crystallographic faceting. The diffraction pattern included in Figure 3b originates from the center of the aggregate growing toward the left and reflects clearly the misorientations present. As in melt-crystallized PEEK spherulites (and those grown from solution at lower temperatures), here too the *b* unit-cell axis corresponds to the radial-growth direction, while *a* is aligned along the lamellar width.

The typical morphology of spherulites crystallized at high temperatures from the other solvent studied here (i.e., α-chloronaphthalene) is seen in Figure 4 to be very similar to that described above. The source of misorientations is related to the profuse initiation of growth at multiple points along the peripheries of these crystals. Thus, what appear initially as broader lamellae in Figures 3 and 4 (with widths of the order of 0.5 μm) are in actuality composites of much narrower microcrystallites growing in the same general direction but under varying degrees of misorientation.

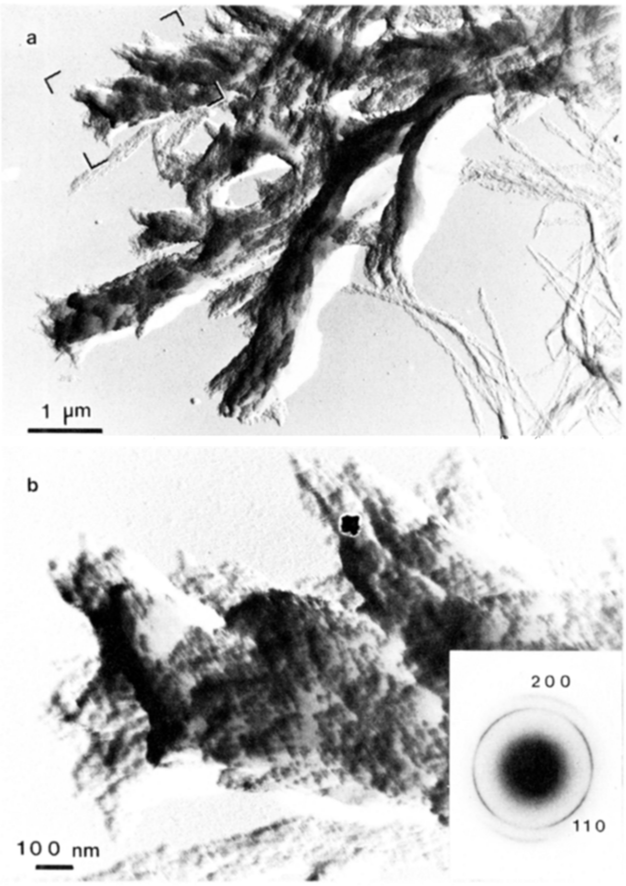

Figure 3. (a) Typical appearance of growth tips of PEEK spherulites crystallized at 220 °C from a 0.01% solution in benzophenone. The narrower crystals at the right were grown during subsequent cooling of the solution to room temperature. (b) Detail of the framed area in (a) at higher magnification. The electron-diffraction pattern shown originates from a ca. 0.5-μm-diameter area at the center of the broad lamella growing toward the left.

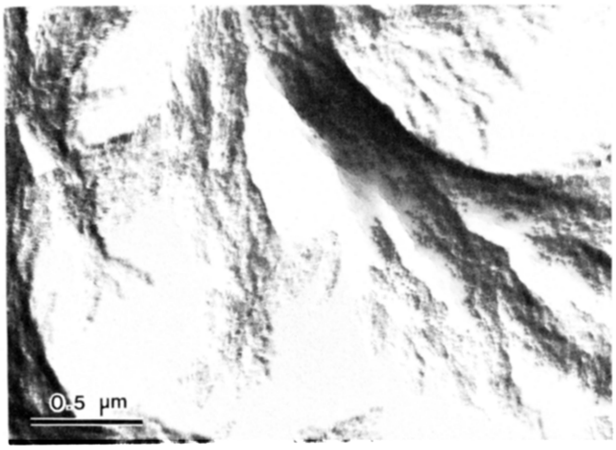

Figure 4. Typical appearance of spherulitic growth tips obtained during crystallization of PEEK from α-chloronaphthalene at 220 °C.

Single Crystals. Isolated single-crystal-like entities were obtained from both solvents at concentrations of 0.01% or less and crystallization temperatures extending up to 220 °C. The morphological characteristics of these crystals fell within two general categories, as described already for spherulites: Long, spearlike crystals for growth temperatures below ca. 215 °C, with shorter and broader counterparts obtained at crystallization temperatures above ca. 215 °C. The appearance of the first is seen in Figure 5, parts a (for benzophenone) and b (for α-chloronaphthalene). In both cases, the crystals are highly elon-

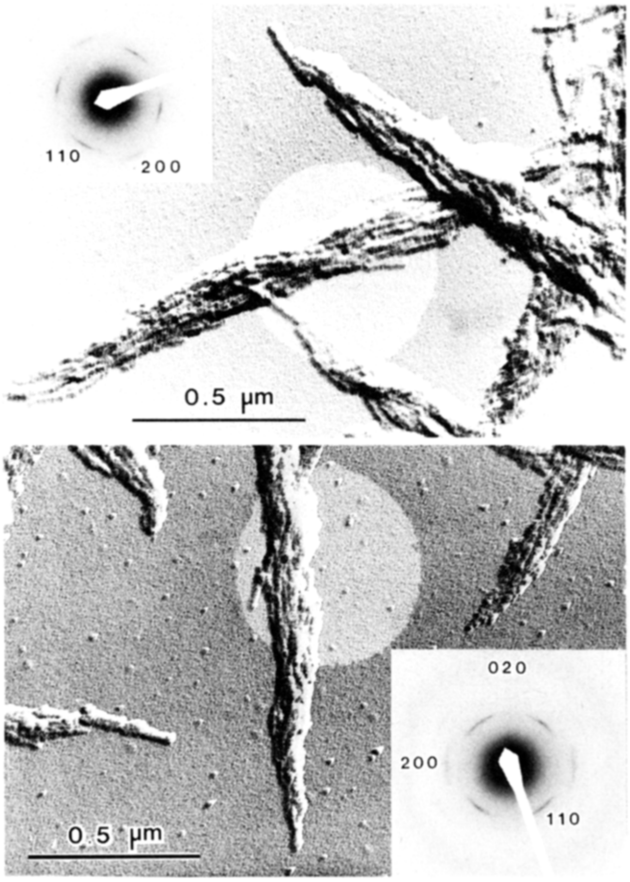

Figure 5. Electron-microscopic appearance of PEEK single crystals grown from a 0.01% solution in (a) benzophenone at 210 °C, and (b) α-chloronaphthalene at 205 °C. The electron-diffraction patterns originate from the circled areas of the micrographs and are shown in correct orientation.

gated and spearlike and show great similarity to the spherulitic lamellae grown at the same temperatures. These crystals vary in length from ca. 1 to 3 μm and in width from ca. 0.1 to 0.3 μm. There is no faceting on a macroscopic scale (some evidence for microfaceting will be given later), and the overall morphology appears distinctly disordered. In fact, individual microcrystallites are clearly discernible within each spearlike lamella; as in the spherulites, they are generally elongated parallel to the long axis of the lamella. Their width is only ca. 15–20 nm, which is remarkable in that it is essentially commensurate with their thickness (ca. 10–15 nm). Therefore, the spear-shaped lamellae are not truly single crystals but rather aggregates of much smaller microcrystallites that have grown in a predominantly aligned manner.

The electron-diffraction patterns included in Figure 5 show both the single-crystal-like nature of the spear-shaped lamellae grown from the two solvents as well as the inherent misorientations of the constituent microcrystallites. The first of these is evident in the *hk*0 identification of all observed reflections, while the second is clearly deduced from their high arcing. The spearlike morphology of our PEEK single crystals, the absence of macroscopic faceting, the extensive misorientations, and the accompanying arcing of their *hk*0 reflections are all analogous to the situations presented by such disordered crystals as branched polyethylene[22] or polyacrylonitrile.[23] In both of these polymers, the disorder is attributable to molecular origins, i.e., the chain branches in polyethylene and the ladderlike linkages in polyacrylonitrile. While a similar cause might also be present in PEEK as a result of the likelihood of isomorphous placement of carbonyl and ether groups[1,5,6] the detailed packing scheme of PEEK chains has not yet been fully resolved.[9]

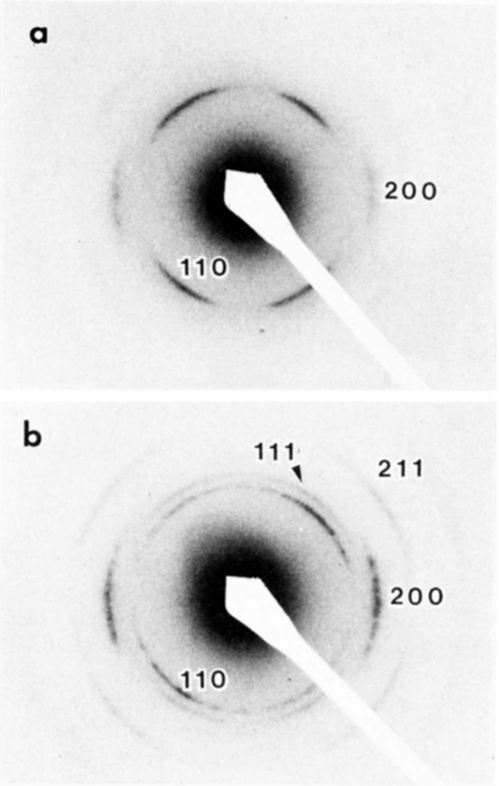

Figure 6. Electron-diffraction patterns from the same single crystal of PEEK grown at 210 °C from a 0.01% solution in benzophenone (a) with the electron beam normal to the lamellar surface, and (b) after a ±31° tilt of the crystal about the *a*-axis.

The long axis of PEEK crystals from benzophenone and α-chloronaphthalene is seen in Figure 5 to correspond to the *b* axis of the unit cell, while their transverse direction corresponds to the *a* axis and the thickness direction to the molecular *c* axis. In order to confirm these assignments in the absence of reflections with a nonzero *l* index, we have examined the three-dimensional variation of the electron-diffraction pattern of a PEEK crystal by tilting in the electron microscope about the *a* axis. Our results are seen in Figure 6. From the reciprocal-lattice construction, using the unit-cell parameters from the literature,[5,6] we calculate that a tilt of 30.9° about the *a* axis should bring the $\{h11\}$ planes to the reflecting position. Indeed, the 111 and 211 reflections are visible in Figure 6b as a result of a 31° tilt (about a horizontal axis) of the same crystal that yields the diffraction pattern of Figure 6a in the untilted position. The slight intensification of the 200 reflection and the residual presence of the 110 in Figure 6b are attributed to misorientations away from the basal plane. Our results from electron-diffraction analysis of single-crystal-like entities of PEEK confirm the unit-cell structure determined from X-ray studies of oriented polycrystalline specimens[5,6] (the suggested tripling[9] of the unit cell along *c* depends upon the extent of isomorphous placement of carbonyl and ether groups, which is still an unresolved question). Our results showing the longitudinal and transverse directions of these PEEK crystals to correspond to the *b* and *a* axes, respectively, are also in agreement with our previous findings from melt- and solution-grown spherulites of this polymer.

The individual microcrystallites comprising the spear-shaped lamellae are not fully discernible in Figure 5 because of the relatively low magnification and the presence of many overgrowths. Figure 7 is a much higher magni-

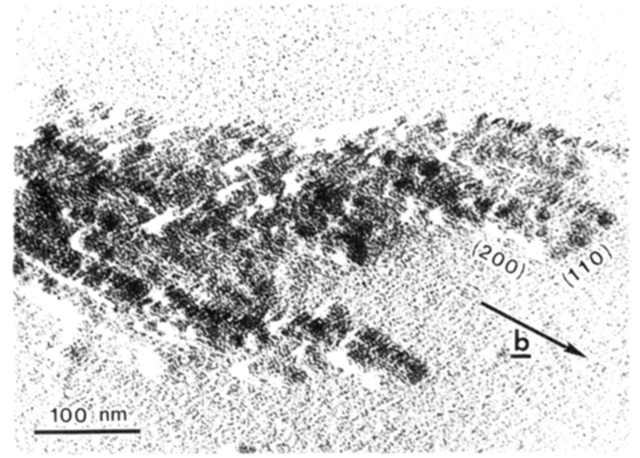

Figure 7. High-magnification appearance of growth tips of a PEEK crystal grown from a 0.01% solution in α-chloronaphthalene at 210 °C.

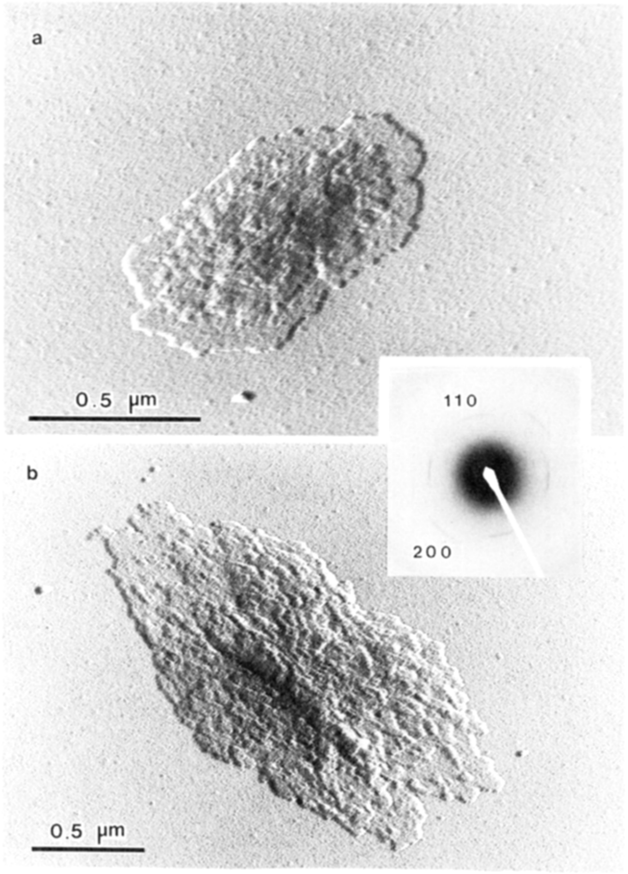

Figure 8. Typical appearance of PEEK single crystals grown at high temperatures (220 °C) from a 0.01% solution in (a) benzophenone, and (b) α-chloronaphthalene.

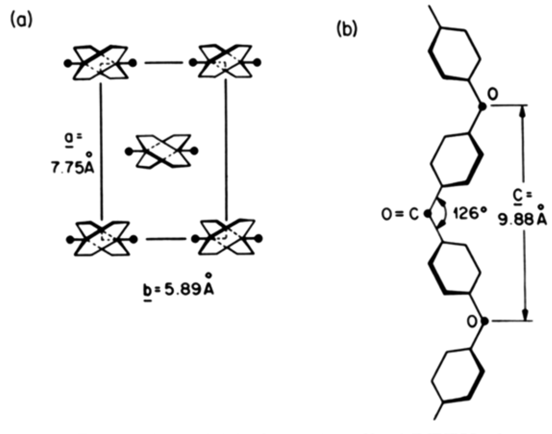

Figure 9. Projection of (a) the unit cell of PEEK along the c axis, and (b) of the molecular conformation of PEEK along the a axis.

fication bright-field electron micrograph of some growth tips in solution-crystallized PEEK, where overgrowths have not yet obscured the morphology of individual microcrystallites. Even though these are indeed elongated in the growth direction, longitudinal discontinuities are also profuse. Moreover, this micrograph also indicates the type and scale of microfaceting that has been observed in PEEK crystals grown at temperatures below ~215 °C. As has been noted from the preceding electron micrographs, crystals of PEEK crystallographically faceted on a macroscopic scale are essentially absent at these growth temperatures. Figure 7 demonstrates that, while *microfaceting* is indeed present to some extent, it occurs only on a very fine scale (i.e., less than ~100 nm). The average measured angle of the better defined microfacets in Figure 7 is 55.5°, from which (based also on the known b growth direction) we can identify these as (200) and {110} (the corresponding calculated angle is 52.8°).

As the crystallization temperature is increased beyond ~215 °C, the crystals become progressively less anisometric through both a decrease of their lengths and an increase of their widths. Typical crystals obtained at 220 °C are seen in Figure 8; their aspect ratios (length/width) are ~2, compared to ~10 at 210 °C. As is shown by the electron-diffraction pattern in this figure, both the crystallographic phase and the unit-cell orientation remain the same as in the crystals grown at lower temperatures. Multilayer formation still occurs extensively and microfaceting continues to be profuse, with (200), (020), and {110} microfacets clearly distinguishable.

In an attempt to understand the origins of the morphological characteristics of solution-grown single crystals and spherulites of PEEK, we examine the molecular conformation and chain packing in Figure 9. The unit-cell dimensions are taken from ref 6. The intramolecular repeat reflects an extended backbone[1,5,6] in which the ether and carbonyl groups define a planar zigzag (see Figure 9b). The phenyl rings are inclined in an alternating manner to the backbone plane, the angle of inclination being assumed to lie in the 40–45° range (by analogy with PPO[7] and PPS[8]). The packing scheme of these chains (which is based again on PPO[7] and PPS[8] and is consistent with our electron-diffraction results) is depicted schematically in Figure 9a: the molecules are located at the corners and center of an orthorhombic unit cell in such a manner that the backbone zigzag planes are parallel to the b axis.

The manner in which these molecules are arranged within the crystals is depicted in a highly schematic manner in Figure 10 (here, straight lines are used to represent the c-axis projections of the molecular backbones). The fact that these backbones are all aligned in the b direction, coupled with the existence of favorable nucleation planes [{110} and possibly (020)], should favor growth along this direction, as is indeed observed. This arrangement of the chain zigzag should also render the (200) planes more susceptible to cleavage and misorientations (e.g., through stresses at growth fronts) and therefore contribute to the restricted widths, fragmentation, and slight mutual misorientation of PEEK crystals that is clearly seen in our micrographs. Similar molecular or packing characteristics also exist in other polymers that exhibit uncommonly narrow, elongated crystal habits. For example, the chain conformation and unit cell in PPS are entirely analogous to those of PEEK and so is also the

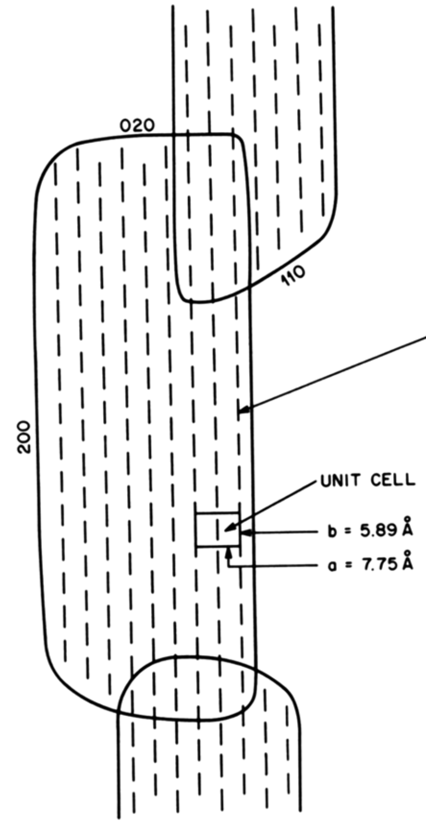

Figure 10. Schematic packing arrangement of PEEK molecules within its single crystals.

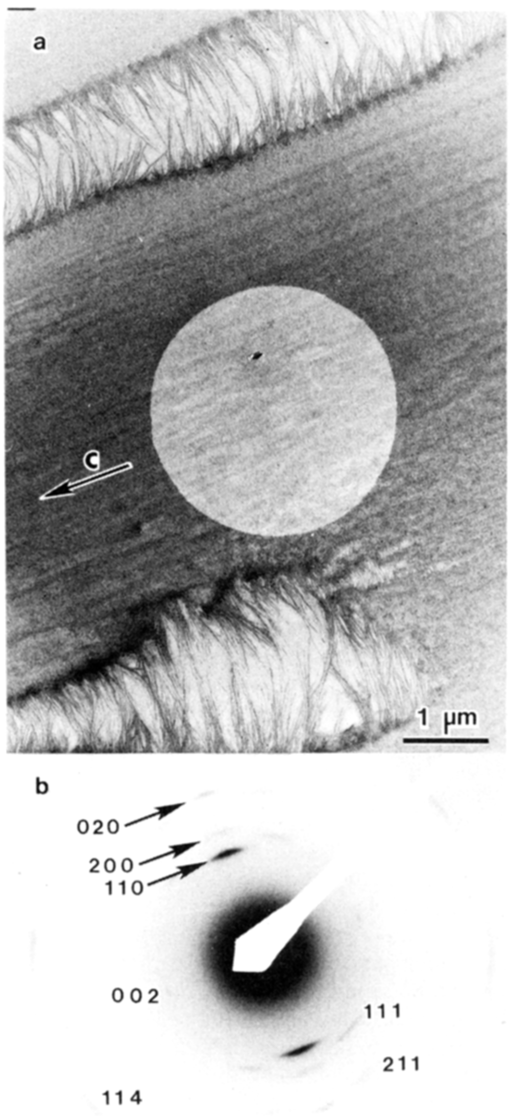

Figure 11. (a) Morphological appearance of PEEK prepared by flow-induced crystallization on a mica substrate from a 0.1% solution in benzophenone; the flow direction is arrowed. (b) Electron-diffraction pattern from the area outlined in (a).

morphology of its spherulites and single crystals;[20] in nylons 66 and 610 and in barium polyglutamate, the molecules are contained in hydrogen-bonded sheets that are arranged parallel to the crystal-growth direction,[19] and in isotactic polypropylene the (040) planes—which are aligned in the direction of crystal growth[24]—are poorly interdigitated on one of their sides.[25]

Flow-Induced Crystallization. So far, we have described morphologies of PEEK crystallized from quiescent solution. Crystallization during flow is also of interest because of the important shish-kebab-like morphologies that it produces both from solution[26] and from the melt;[27] moreover, flow-induced crystallization is associated with processing for some applications of PEEK (such as thin-fiber coatings[2,3]). To obtain some indication of the morphology of thin films of PEEK crystallized under such flow in contact with a substrate, we rapidly sheared drops of a 0.1 wt % PEEK solution in benzophenone on freshly cleaved mica sheets held at ~300 °C.

Typical morphologies obtained in this manner consist of irregular striations parallel to the flow direction as seen in the central part of Figure 11a. The accompanying electron-diffraction pattern shows that these reflect fiber orientation parallel to the direction of extensional flow. At higher magnifications, shorter striations can also be discerned in the transverse direction; these correspond to lamellae that have been overgrown on the fibrous crystallites. Their identity is clearly confirmed in open areas of the film (such as the top and bottom parts of Figure 11a), in which these overgrown lamellae are seen to grow extensively transverse to the flow direction. Thus, the overall morphology appears to be consistent with the shish-kebab-like structures observed in many other polymers as a result of flow-induced crystallization.[26-28]

However, the influence of the substrate manifests itself in a departure from the macroscopically cylindrical crystallographic symmetry about the flow direction that normally characterizes such aggregates of shish kebabs. This is seen by comparison of the intensities of reflections in Figure 11b with those of a uniaxially oriented (mechanically drawn) PEEK film (Figure 12a). In the latter specimen, in which cylindrical symmetry prevails, the 200 reflection appears to be almost as intense as the strongest reflection (i.e., the 110); the 020 reflection, on the other hand, is among the weakest. These crystallographic characteristics are also in agreement with results from unoriented specimens, such as in Figure 12b. To the contrary, the electron-diffraction pattern of the sample obtained by flow-induced crystallization on a planar substrate (Figure 11b) shows a marked increase in the intensity of the 020 reflection, accompanied by a very major decrease in that of the 200—to the extent that the latter is now the weakest of the three equatorial reflections. This is interpreted as a clear departure from cylindrical symmetry in such a way as to render preferentially the *a* crystallographic axis perpendicular, and the *b* axis parallel, to the substrate. This is not surprising in view of our previous results from melt-crystallized PEEK,[15] which showed that even during quiescent growth from the melt

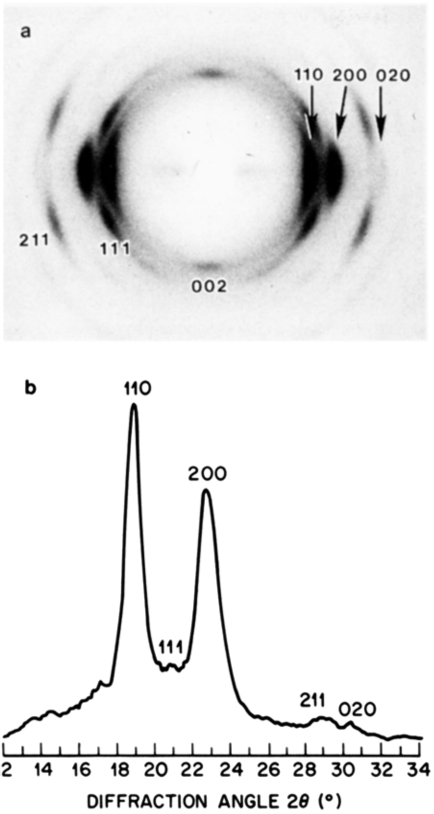

Figure 12. (a) X-ray diffraction pattern of uniaxially oriented PEEK, mechanically drawn 3:1 in the vertical direction; (b) X-ray diffractogram of unoriented, melt-crystallized PEEK.

the *bc* plane is the one that is preferentially nucleated on the substrate. This may be explained by the fact that alignment of the molecule with the *bc* plane parallel to the substrate maximizes the interfacial area of contact and may thus reduce the free energy for nucleation (see also Figure 9a). Such preferred alignment of PEEK molecules during extensional flow on a substrate occurs consistently not only in small areas (e.g., of the order of $\sim$2.5 μm delineated in Figure 11a) but essentially throughout the specimen. This is markedly different from the usual situation during flow-induced crystallization,[28] in which there is no crystallographic coherence *between* shish kebabs and in which any coherence *along* the fibrillar direction is preserved to only a fraction of a micrometer at most.

Conclusions

Solution crystallization of PEEK from both α-chloronaphthalene and benzophenone yielded similar spherulites and single crystals possessing very narrow, elongated habits and exhibiting microfragmentation and disorder. The preferred growth direction of both single crystals and spherulitic lamellae corresponds to the *b* crystallographic axis and the molecules are normal to the lamellar surfaces. These results are consistent with our earlier findings from melt-grown PEEK. Flow-induced crystallization of thin films on a substrate was shown to yield uniquely oriented fibrous-lamellar composites showing preferred disposition of the *c* axis parallel to the flow direction, of the *b* axis in the plane of the substrate, and of the *a* axis normal to that plane. These features, as well as the narrowness and microfragmentation of PEEK lamellae and single crystals, were attributed to the anisometric molecular profile and the packing scheme of chains within the unit cell (as well as their interaction with the substrate in the case of flow-induced crystallization).

Registry No. PEEK, 31694-16-3.

References and Notes

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