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Morphology and structure of poly(aryl ether ketone ketone) containing isophthaloyl moieties crystallized from dilute solution

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Spherulites and lamellar single crystals of poly(aryl ether ketone ketone) containing isophthaloyl moieties (PEKK(I)) were obtained from dilute α-chloronaphthalene solution. The morphology and structure of the spherulites and single crystals were studied by electron microscopy and electron diffraction. The spherulites were found to consist of elongated lamellar branches that grow with the *b* crystallographic axis in the radial direction. Single crystals possess a similar habit, with *b* parallel to the long axis, *a* transverse, and *c* perpendicular to the lamellae plane. High-resolution images of the PEKK(I) crystals which show the perfection of and defects in the crystals, were obtained, and many defects or dislocations were observed. © 1997 Elsevier Science Ltd.

(Keywords: poly(aryl ether ketone ketone); solution crystallization; morphology)

Introduction

In recent years, high-performance polymers have already been the focus of scientific and industrial studies all over the world. A large number of works on crystal structure, morphology, thermal and mechanical properties, and blends can be found in the literature. Poly(aryl ether ketone ketone) (PEKK) is one of the most common members of a new class of high-performance engineering thermoplastics, the poly(aryl ether ketones). Poly(aryl ether ketone ketone) containing isophthaloyl moieties, PEKK(I), whose repeat chemical structure is shown in *Scheme 1*, has a melting temperature of around 310°C and a glass transition temperature of around 155°C[1]. Molded specimens of PEKK(I) have been examined by optical microscopy, differential scanning calorimetry, X-ray techniques, and electron diffraction[2,3]. X-ray diffraction on uniaxially oriented samples, combined with selected-area electron diffraction experiments on partly oriented crystals, showed the unit cell to exhibit orthorhombic packing ($a = 0.766$ nm, $b = 0.611$ nm, $c = 1.576$ nm) and to be very similar to those of other linear aromatic polymers, such as poly(*p*-phenylene oxide) (PPO) and poly(*p*-phenylene sulfide) (PPS)[4,5].

One characteristic of the poly(aryl ether ketone) series of major importance in terms of performance, processability and structural characterization is its exceptional chemical resistance. Almost all poly(aryl ether ketones) are described as being insoluble in all common solvents with the exception of strong acids. The most effective solvents have been found among the diaryl sulfones[6], pentafluorophenol [7], and others. Recently, Lovinger and Davis have succeeded in dissolving PEEK in α-chloronaphthalene and benzophenone. From these solvents, ultrathin films were cast, and spherulite and lamellar single crystals were obtained. Their resulting structure and morphology, as revealed by electron microscopy and electron diffraction, have been reported[8–10].

Recently, we have extended the solution-crystallization studies to the PEKK species, and have succeeded in obtaining lamellar single crystals of poly(ether ketone ketone) containing isophthaloyl moieties, PEKK(I). In this communication, we describe our results of a structural and morphological investigation of spherulites and single-crystal-like lamellae obtained from α-chloronaphthalene.

Experimental

Sample preparation. The sample used was developmental grade PEKK provided by DuPont Co. The polymer was dissolved in α-chloronaphthalene (reagent grade from Fischer Scientific, with $T_b = 263$°C) to give a concentration of 0.02% by weight for crystal growth. The dissolution temperature of PEKK in α-chloronaphthalene is about 180°C. A gradual process was adopted for the crystallization of PEKK(I). A mixture of polymer and solvent in a sealed tube was heated to 180°C under a nitrogen atmosphere, and held at this temperature for about 5 h until the polymer was completely disssolved. The polymer solution was then cooled to 100°C at about 0.1°C min^{-1} (for about 1 week). A drop of the resulting suspension was deposited on freshly cleaved mica coated with a carbon supporting film. The carbon films with the PEKK suspensons on mica were dried for 1 day in a vacuum oven at 100°C and then floated off in water and picked up on copper grids.

Electron microscopy. The specimens were examined without shadowing with a Hitachi H-600-2 electron microscope (LaB_6 filament) which was operated at 100 kV with a side-entry goniometer and a liquid nitrogen anti-contamination trap. The images were recorded on photographic plates. Electron diffraction measurements were made using the selected-area diffraction method. Electron diffraction diagrams were calibrated with gold.

A JEOL JEM-2010EX electron microscope (LaB_6 filament), which was eqipped with a minimum dose system (MDS) and operated at 200 kV with a side-entry goniometer and a liquid nitrogen anti-contamination trap, was also used to obtain the high-resolution lattice images.

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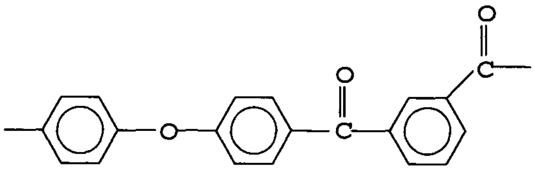

PEKK(I)

Scheme 1 Repeat chemical structure of poly(aryl ether ketone ketone) containing isophthaloyl moieties (PEKK(I))

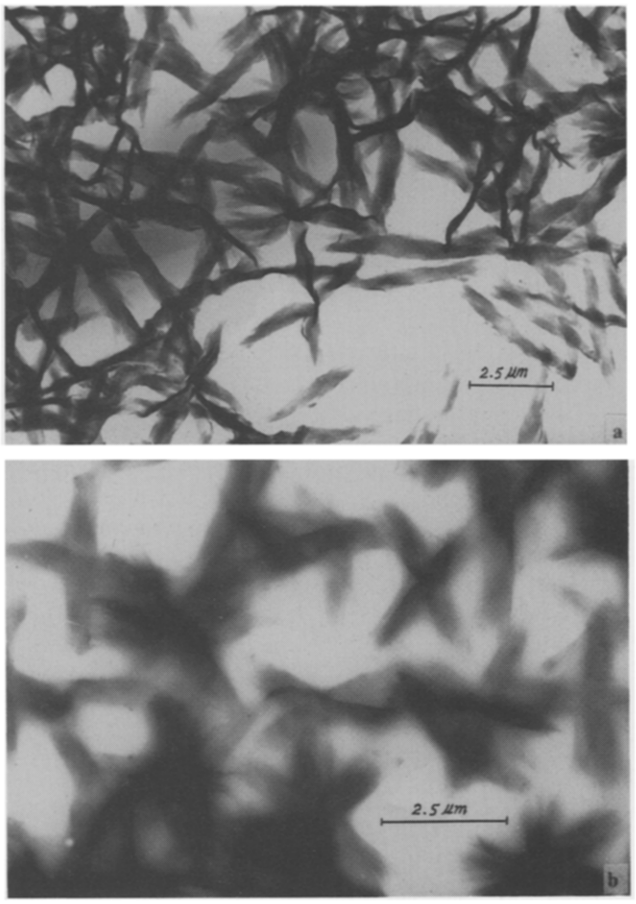

Figure 1 Bright-field morphology of PEKK(I) crystallized from 0.02% α-chloronaphthalene solution. (a) A coarse spherulite composed of seemingly fibrillar but narrow lamellar crystals; (b) the sheaf-like appearance of the crystals. The constituents are lamellae

The spherical aberration coefficient (C_s) was 1.0 mm. A condenser aperture of 120 μm was employed and a spot size '3' was selected. The high-resolution electron microscopy (HREM) images were recorded on photographic plates at a direct magnification of 400 000 × .

Results and discussion

The PEKK crystals were grown by means of a gradual procedure in a 0.02% α-chloronaphthalene solution under a nitrogen atmosphere. From this solution, coarse spherulites and single-crystal lamellae were obtained. We describe below the morphological types obtained in our studies and the defects in the PEKK crystals.

Morphology of PEKK(I) crystals. The typical appearance of the PEKK(I) crystals is shown in *Figure 1. Figure 1a* shows a coarse spherulite whose textural constituents are seemingly 'fibrillar' but very narrow lamellar crystals. This morphololgy is very similar to that of PEEK which was reported by Lovinger and Davis[10], who proposed that the morphological growth was homogeneously nucleated. The other morphology demonstrated in *Figure 1b* corresponds to a sheaf-like appearance which was heterogeneously nucleated and whose constituent narrow lamellae radiated out from its centre. In any case, the coarse spherulite may be an immature bundle of PEKK(I) narrow lamellar crystals. The most significant characteristic of the PEKK(I) spherulites lies in their lamellae. The radial growth direction of these PEKK(I) spherulites corresponds to the *b* crystallographic axis, while the unit-cell axis, *a*, corresponds to the transverse growth direction. Lovinger and Davis[8–10] have found similar long and narrow lamellae growing in the *b* direction during their study of PEEK. Similar morphologies have also recently been revealed by Cheng and co-workers[3,4] during their study of PEKK crystallized from the melt. Such features from both the melt and solution crystallization suggest that the lamellar habit is an inherent characteristic of this polymer.

Single-crystal-like lamellae have been isolated successfully from the suspension of PEKK(I) in α-chloronaphthalene. The morphological characteristics of these crystals are shown in *Figure 2*. In this case, the crystals show great similarity to the spherulite lamellae. The overall morphology appears distinctly ordered.

The electron diffraction pattern included in *Figure 2* shows the single crystal nature of the lamellae as well as the inherent orientation. Reflections of (010), (020), (210), (110) and (200) are observed. Thus, the PEKK(I) molecular stems are oriented normal to the supporting-film surface. The long axis of PEKK(I) crystals corresponds 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. The reflection index from the electron diffraction analysis of single crystals confirms the unit cell structure determined by X-ray studies. These results are also in agreement with previous results from melt- and solution-grown crystallites of PEEK and from melt-grown crystallites of this polymer.

HREM images and crystal lattice defects. Modern elec-

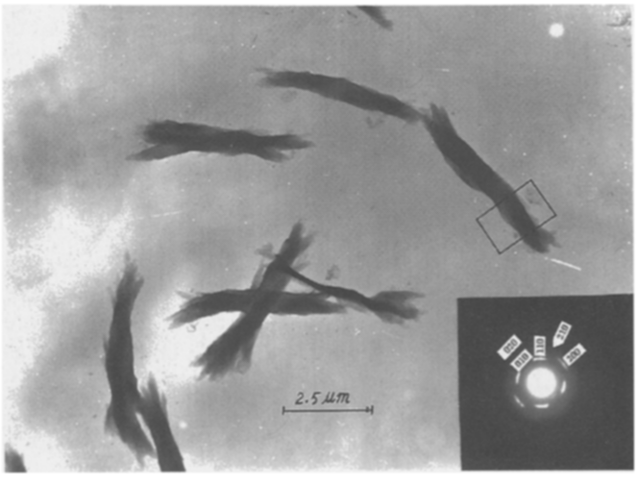

Figure 2 Morphology of the single-crystal-like lamellae of PEKK(I) crystallized from 0.02% α-chloronaphthalene solution

tron microscopes are capable of such high resolution that the direct observation of crystal structure is possible on a molecular or atomic level. The information acquired by HREM provides correct evidence for ascertaining whether the motifs array crystallographically, as predicted by X-ray diffraction and other spectroscopic means. In research and applications, it is considered that the properties and performance of the materials are sensitive to the type, concentration and distribution of the imperfections that they possess. HREM is effective for the elucidation of microstructures and minute defects of crystalline materials when appropriate sample preparation methods are adopted. In the present work, observation of the microstructure by HREM will prompt a discussion of the defects.

The phase-contrast transfer function was used to obtain contrast variations, enabling lattice planes to be imaged. Phase contrast is produced by the interference of the scattered electron wave that passes through the aperture with the unscattered or background electron wave; this technique has been described previously by Voigt-Martin and Durst[11,12].

A series of experiments involving TEM observations on the crystals have shown that the PEKK(I) crystals are less sensitive to electron irradiation, so we can take a clear photograph of its lattice structure image. *Figure 3* shows the resulting high-resolution electron micrograph of the PEKK(I) crystal. Close observation in some directions reveals one-dimensional lattice fringes with a spacing of 0.308 nm, corresponding to the (020) lattice plane. The electron diffraction pattern of the sample shows a (020) reflection corresponding to a lattice spacing of 0.306 nm. These strong 0.308 nm lattice fringes provided unambiguous evidence for local perfections of the crystalline registry and order possible in PEKK(I) crystals. A possible explanation for this phenomenon could be that a different orientation of the (020) lattice planes had occurred in the crystallization process in α-chloronaphthalene solution.

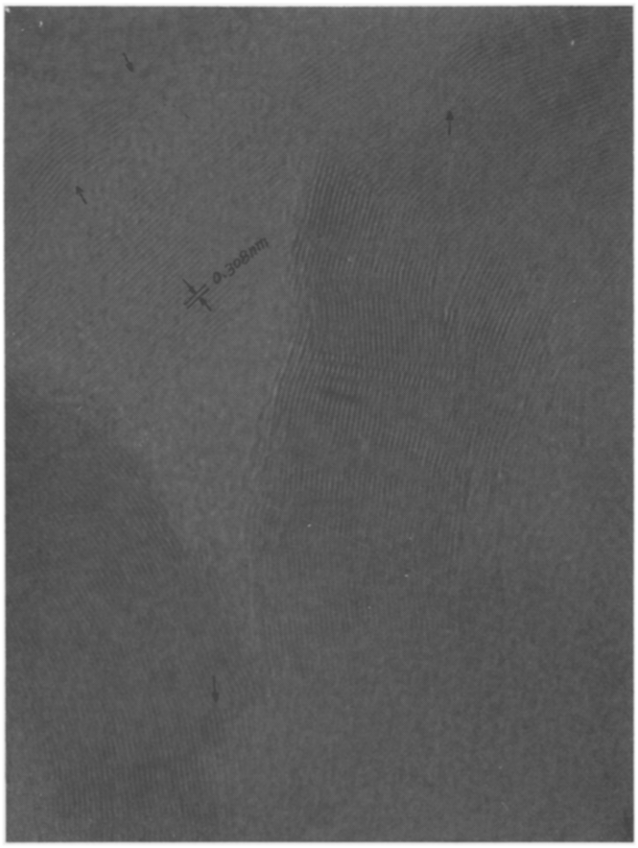

Figure 3 High-resolution electron micrograp of PEKK(I). The (020) lattice can be observed clearly. The arrows indicate the defects in the PEKK(I) crystals. The lattice distance is 0.308 nm

The lattices in the micrograph seem to suggest real chains existing in the crystal. Accordingly, we interpret the micrograh on the basis that perfect lattices reflect a high order of the chain stacking whereas distorted ones (indicated with arrows) and chaotic regions reveal the presence of imperfections and an amorphous state in the real crystal. It is recognizable that edge dislocations appear in the PEKK(I) crystals. These dislocations should be accompanied by a stacking fault. For the crystal lamellae of PEKK(I), lamellar branching or bending caused by this type of dislocation may take place. Thus, it may be deduced that this type of edge dislocation is one of the origins of lamellar branching or bending as well as a cause of mutual misorientation of adjoining crystals. Similar results concerning misorientation and dislocations have been reported by Tsuji *et al.* in their investigation on solution-grown PEEK crystals using HREM[13,14]. A more detailed discussion of the nature and origin of this phenomenon must, however, await systematic study, and a further meticulous investigation is proceeding.

Conclusion

The crystallization of PEKK(I) was carried out successfully from dilute α-chloronaphthalene solution. Sheaf-like or transmitting spherulites and lamellar crystals are features characteristic of PEKK(I) crystallized from dilute solution. The growth direction of the crystals is along the direction of the *b* axis, and the *a* axis is transverse to the growth direction and lies on the lamellar plane. The *c* axis is perpendicular to the crystal lamellae. The (020) lattice images of PEKK(I) were obtained. The lattice fringe direction is slightly varied and some of the lattice fringes were curved in a particular place, the lattice distortion being accompanied by the bending of the stems in the crystallite.

Acknowledgements

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References

1. Gardner, K.H., Hsiao, B.S. and Matheson, R.R. Jr. et al., *Polymer*, 1992, **33**, 2483.
2. Hsiao, B.S., Gardner, K.H. and Cheng, S.Z.D., *J. Polym. Sci., Part B*, 1994, **32**, 2585.
3. Ho, R., Cheng, S.Z.D., Hsiao, B.S. and Gardner, K.H., *Macromolecules*, 1995, **27**, 1938.
4. Ho, R., Cheng, S.Z.D. and Fisher, H.P. et al., *Macromolecules*, 1994, **27**, 5787.
5. Dawson, P.C. and Blundell, D.J., *Polymer*, 1980, **21**, 577.
6. Attwood, T.E., Dawson, P.C. and Freeman, J.L. et al., *Polymer*, 1981, **22**, 1096.
7. Ho, R., Cheng, S.Z.D., Hsiao, B.S. and Gardner, K.H., *Macromolecules*, 1994, **27**, 2136.
8. Lovinger, A.J. and Davis, D.D., *J. Appl. Phys.*, 1985, **58**, 2843.

9. Lovinger, A.J. and Davis, D.D., *Macromolecules*, 1985, **26**, 322.
10. Lovinger, A.J. and Davis, D.D., *Macromolecules*, 1986, **19**, 1861.
11. Voigt-Martin, I.G. and Durst, H., *Liq. Cryst.*, 1987, **2**, 6011.
12. Voigt-Martin, I.G. and Durst, H., *Macomolecules*, 1989, **22**, 168.
13. Tsuji, M., Kawamura, H. and Kawaguchi, A. et al., *Bull. Inst. Chem. Res., Kyoto Univ.,*, 1989, **67**(2), 77.
14. Tsuji, M. and Kohjiya, S., *Prog. Polym. Sci.,*, 1995, **20**, 259.