

Crystal morphological investigation in thin films of poly(aryl ether ketone ketone) having a *meta*-linkage

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The lamellar crystal morphology of thin films of poly(aryl ether ketone ketone) having a *meta*-linkage (PEKK(I)) is observed under transmission electron microscopy (TEM), utilizing samples with different thermal histories and preparation procedures. After isothermal crystallization from the melt, a double endothermic behaviour can be found through differential scanning calorimetry (d.s.c.) experiments. Partial melting of PEKK(I) can be obtained by heating the samples to a temperature between these two endotherms. By comparing the TEM morphological observations of the samples before and after partial melting, it can be shown that edge-on lamellar crystals, having different thermodynamic stabilities, form during isothermal crystallization. After partial melting, only the type of lamellar crystal exhibiting the higher thermodynamic stability remains. Small angle X-ray scattering (SAXS) results exhibit a change in the long period of the lamellar crystals before and after the partial melting process. For the solution-induced crystallization of PEKK(I), only a single endotherm exists in the d.s.c. observations. After annealing at high temperatures, however, a double endothermic behaviour appears. This also results in a decrease in the long period observed by SAXS. The double population of the lamellar crystals is difficult to observe in TEM, since the lamellar crystals in these thin film samples possess a random, rather than an edge-on, orientation. Detailed TEM imaging for observing these lamellar crystals is discussed. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Since the first differential scanning calorimetry (d.s.c.) study of poly(aryl ether ether ketone) (PEEK) by Blundell and Osborn¹, there has been a great deal of discussion and controversy about the origin of the double endothermic behaviour observed during the heating of PEEK samples after isothermal crystallization from the melt or glassy state. This double endothermic behaviour refers to the fact that a low endotherm is generally observed about 10°C to 30°C above isothermal crystallization temperatures, whereas a high endotherm, which is less sensitive to the relatively low crystallization temperatures, increases only when the crystallization temperature becomes high². In general, the higher the crystallization temperature and the longer the annealing time, the greater the increase of the low endothermic peak. Multiple endothermic behaviour has also been obtained when samples are cooled in steps for crystallization³.

Although it is generally agreed that these two endothermic peaks are associated with crystal melting, various models have been proposed in order to explain this behaviour. Most popular models involve either a single

population, or a double population of thickness in the lamellar crystal morphology (SPC and DPC). To illustrate the double endothermic behaviour, the SPC model requires a melt/recrystallization process during heating after PEEK has been isothermally crystallized^{1,4}. The formation of the crystals which are attributed to the high endothermic peak result from the melting and recrystallization of the crystals which were originally formed during isothermal crystallization to give the low endothermic peak. Blundell reported that increasing the heating rate leads to a shift in the melting temperatures of these two peaks: the low temperature endotherm shifts to higher temperatures and the high temperature endotherm shifts to lower temperatures⁴. This mechanism was further analysed by Porter and coworkers^{5,6}. An overlap of the low temperature endotherm and the crystallization exotherm results in an apparent small, low temperature endotherm. The structural changes of PEEK, crystallized from the glass, during subsequent heating and cooling processes were monitored using combined small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) methods. These results have been interpolated to support the SPC model⁷.

On the other hand, the DPC model assumes that at a constant crystallization temperature, two PEEK lamellar

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crystal morphologies having different metastabilities are formed. Both recrystallization and reorganization of these crystals occur during heating². Using the replica method in transmission electron microscopy (TEM), Bassett *et al.* observed that the melting peaks are associated with two distinct crystal morphologies through which the crystallization of the bulk PEEK takes place first by the growth of dominant thicker lamellae and subsequently by infilling thinner lamellae⁸.

Time-resolved synchrotron SAXS was employed to investigate crystallization behaviours by Wang *et al.*⁹, by Hsiao *et al.*^{10,11} and by Kruger and Zachmann¹². Their experimental evidence also appears to be in favour of the proposed DPC model. In general, the long period determined by time-resolved SAXS studies decreases with increasing isothermal crystallization time. However, the long period increases after the melting of the low endothermic peak during heating. This result suggests that the initial isothermal crystallization produces a greater long period, and the later crystallization produces a smaller one. The melting of the low endothermic peak through the melting of the thinner crystals results in an increase of the long period.

More recently, a proposal of dual lamellar thickness was suggested by Marand and coworkers^{13,14}. They assume that thinner lamellae are present in separate stacks instead of infilling between the thicker lamellae. In the early stage of crystallization, lamellar stacks consisting of thicker lamellae form from the melt and the region in-between these lamellar stacks simultaneously creates pocket-like amorphous areas called 'liquid pockets'. Later, lamellar stacks with thinner lamellae form in these liquid pockets. These stacks have the same amorphous layer thickness, but exhibit a different long period, based on the SAXS data. The existence of these dual lamellar thicknesses in different stacks could be related to the double endothermic behaviour.

Another TEM observation presented by Lattimer *et al.* reported that on heating samples which possess two lamellar populations to a temperature between the two melting endotherms, the thinner crystals are seen to be molten while the thicker crystals are unaffected by this process¹⁵. However, these smaller crystals appear in the regions between the spherulites. Thus, in the DCP model, the location of the two crystalline populations is still under discussion.

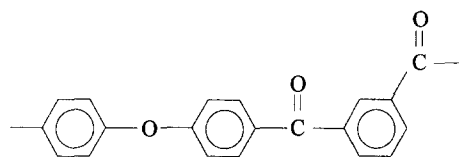
Poly(aryl ether ketone ketone) having a *meta*-phenylene linkage, PEKK(I), crystallizes much slower compared to PEEK. This polymer provides a broad crystallization time window, which is ideal for studying the morphological change during crystallization. It also has a relatively low melting temperature (around 290°C), which prevents thermal decomposition during long isothermal crystallization and annealing. In this paper, the double endothermic behaviour and the corresponding lamellar crystal morphology of PEKK(I) in the thin film form are studied using d.s.c., TEM and SAXS measurements. Different thermal histories of isothermal crystallization from the melt and solvent-induced crystallization experiments are conducted.

EXPERIMENTAL

Materials and samples

PEKK(I) was provided by the DuPont Company for this study. PEKK(I) was prepared from biphenyl ether

(BPE) and isophthalic acid (I) in a two-step process. A detailed description of the synthetic route is given in ref. 16. The number-average molecular weight of the sample is around 7000, and the polydispersity is 3. The chemical structure of PEKK(I) is



Thin PEKK(I) films with thicknesses ranging from 0.01 to 0.1 μm were prepared for TEM observations by casting a 0.1% (w/w) PEKK(I)-pentafluorophenol (PFP) solution onto carbon coated glass slides. The solvent was subsequently evaporated in a vacuum oven. The samples were heated to *ca* 20°C above the equilibrium melting temperature (310°C for PEKK(I)¹⁷) for several minutes, and then either quenched in liquid nitrogen to generate amorphous glassy films for solvent-induced crystallization, or rapidly cooled to a preset temperature for melt-crystallization. For solvent-induced crystallization, the amorphous glassy films were exposed to methylene chloride at room temperature for 1 week. After crystallization, the solvent was evaporated in a vacuum oven at 50°C under reduced pressure for 2 days. Some solvent-induced crystallized samples were further annealed at a preset temperature. After these different crystallization conditions were applied, the films were stripped, floated onto a water surface, and picked up using copper grids.

A partial melting process was also carried out to study the correspondence between the double endotherms and crystal morphology. This process is similar to the study of Bassett *et al.* on PEEK⁸. After completing isothermal crystallization, the crystallized samples were heated from room temperature to 270°C, which is in-between the low endothermic peak and the high endothermic peak, and then quenched into liquid nitrogen. The samples were then prepared for TEM study using the aforementioned procedure.

D.s.c. samples were prepared using the same sample thermal procedure as the TEM experiments. The sample weight was typically 2–3 mg. Samples were encapsulated in hermetically sealed aluminium pans. SAXS samples were prepared in a aluminium cup with size 2 × 2 × 10 mm³. The thermal histories were the same as in the samples used in TEM and d.s.c.

Instrumentation and experiments

PEKK(I) crystal morphology and electron diffraction (ED) patterns were observed via a JEOL (1200 EX II) TEM using a 120-kV accelerating voltage. The PEKK(I) films were shadowed with Pt and coated with carbon for TEM observations. Calibration of the electron diffraction spacing was carried out using Au and TiCl.

Thermal measurements were performed on a Du Pont DSC910. The temperatures and heat flow scales were calibrated using standard materials over a wide temperature range at a heating rate of 10°C min⁻¹. After isothermal crystallization or annealing at a preset temperature, the samples were heated to above the melting temperature without prior cooling.

Synchrotron SAXS experiments were carried out at

the 3A2 beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The X-ray wavelength was 0.154 nm (8.000 keV) and a positional sensitive detector (MBraun) was used to record the scattering patterns. The counter was calibrated with a duck tendon with known spacings. A Lorentz correction was applied by multiplying the intensity, I (counts per second) by s^2 ($s = 2 \sin \theta / \lambda$, where λ is the wavelength of the synchrotron X-ray radiation). The SAXS experiments were conducted at room temperature with samples quenched via liquid nitrogen after the isothermal experiments and partial melting were performed.

RESULTS AND DISCUSSION

Crystal morphologies observed after isothermal crystallization from the melt

PEKK(I) crystallized isothermally from the melt at different crystallization temperatures exhibits two endotherms during heating. In the crystallization temperature range between 150°C and 250°C, a small endothermic peak at a temperature 10–20°C above the crystallization temperature can be observed along with a high endothermic peak with a peak temperature around 286°C. At a constant isothermal temperature, the low endothermic peak temperature and its apparent heat of fusion increase with crystallization time. In order to examine the sequence of crystallization, isothermal crystallization of PEKK(I) at 250°C was studied at different crystallization times. The d.s.c. melting traces were recorded immediately after each crystallization time, and are shown in *Figure 1*. No appreciably low endothermic peak has been found before 25 min of isothermal crystallization time. However, the high endothermic peak develops in the early stages of crystallization. The low endothermic peak appears only after 25 min isothermal crystallization time. The overall crystallization, including the low and high endothermic peaks, is complete after approximately 60 min. With an increase in crystallization time, the low endothermic peak shifts slightly to higher peak temperatures. It is unlikely that complete melting of the low endothermic peak and subsequent recrystallization of the amorphous PEKK(I) to form the high melting endothermic material has occurred due to the slow crystallization rate of PEKK(I) in this temperature region. Note that the crystallization rate of this polymer is at least two orders of magnitude slower than PEKK with all *para*-linkages at the same undercoolings¹⁶. The time needed for PEKK(I) to develop 50% crystallinity is 30 min at 250°C and over 100 min at 270°C. In the d.s.c. heating experiments, the time required to pass through this temperature region to the melting temperature is less than 4 min at a heating rate of 10°C min⁻¹. Therefore, it is doubtful that the high endothermic peak is formed via a recrystallization process of the low endothermic peak materials after melting.

In order to examine a possible difference of the thermal behaviour between the bulk and thin film samples, over 100 thin film samples were prepared and crystallized under a prolonged time period at the same isothermal temperature (250°C). The samples were then collected to obtain a total sample weight of 0.5 mg, and its d.s.c. heating trace was the same as that reported in *Figure 1* at the longest crystallization time. This indicates

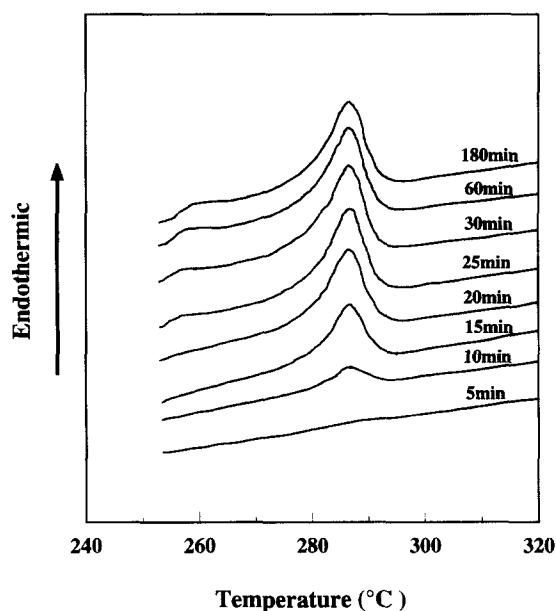


Figure 1 Melting endotherms of PEKK(I) crystallized at 250°C for different times from the melt. All scans are at 10°C min⁻¹ and scanned directly from the crystallization temperature



Figure 2 TEM observations of PEKK(I) edge-on lamellar morphology in spherulites grown from the melt at 230°C for 2 h. An ED pattern is also included

that both the bulk and thin film samples have the same phase behaviour.

Thin films of PEKK(I) crystallized at 230°C for 2 h from the melt show a typical spherulitic morphology consisting of narrow ribbon-like lamellae¹⁷. *Figure 2*



Figure 3 TEM observations of PEKK(I) spherulitic morphology grown from the melt at 230°C for 2 h after partial melting

shows part of a spherulite with edge-on lamellar crystals, as indicated by the ED pattern included in this figure. The long period of these lamellar crystals is estimated to be approximately 10 nm. Two or more layers of lamellar crystals are frequently coupled together. It should be noted that this sample possesses two endothermic peaks in the initial d.s.c. heating trace. After the PEKK(I) sample is heated to 270°C (the temperature between the melting temperatures of the low and the high endotherms) and quenched in liquid nitrogen, only the high endotherm can be found in the d.s.c. heating trace. In TEM observations on samples with the above thermal history, individual lamellar crystals exhibiting a long period of approximately 15 nm are seen, as shown in *Figure 3*. This result seems to indicate that before the partial melting process, two kinds of lamellar crystals exist (*Figure 2*). When the temperature increases to 270°C, one kind of lamella (the thinner) melts, due to its lower metastability. The remaining lamellar crystals may thicken during the 40°C heating process (from 230 to 270°C). Therefore, a population of less stable lamellar crystals may be responsible for the low endothermic behaviour. Similar results can also be observed for PEKK(I) crystallized at 250°C for 5 h from the melt¹⁸.

Further evidence is provided by SAXS experiments. Long periods can be determined after the Lorentz correction. *Table 1* lists the long periods of PEKK(I) crystallized at different crystallization temperatures before and after the partial melting of the samples at 270°C. It is seen that the long period increases with increasing isothermal crystallization temperature in all

Table 1 Long period (determined from the scattering maximum in Lorentz-correction using Bragg's law) for PEKK(I) crystallized at different crystallization temperatures before and after partial melting

Temperature (°C)	Long period before partial melt (nm)	Long period after partial melt (nm)
250	14.5	14.7
230	13.9	14.7
210	12.5	14.7

virgin samples. After partial melting, the long period shows a clear increase as compared to the initial value (see *Table 1*). This result is consistent with the crystal morphology observed via TEM (*Figures 2* and *3*). One possible explanation is the melting of thermodynamically less stable, thinner lamellae in-between the more stable, thicker lamellae. As a result, the residual thicker lamellae increases the long period. It is particularly interesting to find that the long periods of the samples crystallized at different temperatures from the melt essentially reach a constant value after partial melting (*Table 1*). This seems to indicate that the long periods observed after partial melting are determined by the temperature at which the heating process for the partial melting stops (here, at 270°C). At 270°C, the more stable lamellae may thicken until finally only the lamellae having a long period of 14.7 nm survives.

In an ideal case, all of the long periods between the thicker lamellae should be equal, and after partial melting the long periods should be double that of the original values. However, this is not seen in our SAXS experiments. In fact, we have observed lamellae stacks without the coupling morphology (via TEM) in samples without partial melting. Also, the population ratio between the coupled and uncoupled morphologies is less than 50%. Therefore, the long periods determined by SAXS do increase after partial melting, but are not exactly double that of the original long periods. This demonstrates that the population of the thermodynamically less stable lamellae is relatively small as compared to that of the thicker lamellae.

Crystal morphologies observed after solvent-induced crystallization

Methylene chloride can interact with PEKKs and induce swelling to activate the transformation of the amorphous phase into crystals. It is also our goal to study the double endothermic behaviour through this transformation process. First, there is no double endothermic behaviour found after solvent-induced crystallization, as shown in *Figure 4a*. Only after further annealing at temperatures above the glass transition temperature can the double endothermic behaviour be observed (*Figure 4*). One possible explanation for this is that molecular motion in this process is highly limited and localized. After primary crystallization in the presence of methylene chloride, molecular chains may not have enough mobility to initiate the second stage in crystallization (i.e. the growth of thinner lamellae).

After solvent-induced crystallization, randomly arranged lamellae having small sizes can be observed in PEKK(I) thin film samples under TEM, as shown in *Figure 5*. However, no significant evidence for the coupled lamellar morphology can be found. After further annealing at a temperature of 250°C for 5 h, the distribution of the crystal size becomes slightly broadened and the average

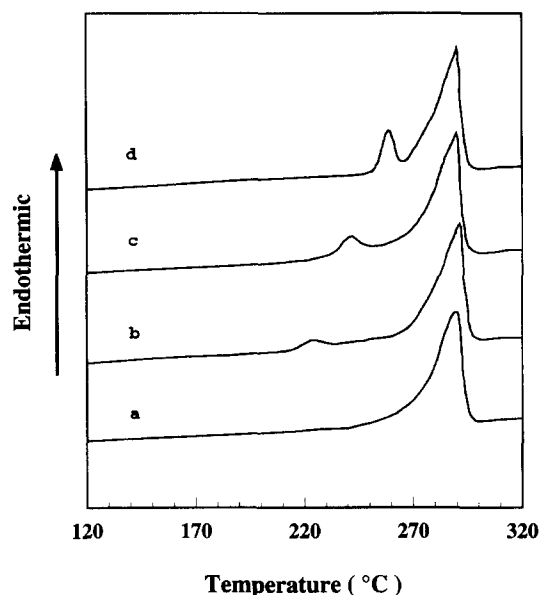


Figure 4 Melting endotherms of PEKK(I) crystallized via solvent-induced crystallization: (a) without further annealing; (b) annealing at 230°C for 2 h; (c) annealing at 250°C for 5 h. All scans are at 10°C min⁻¹

Table 2 Long period (determined from the scattering maximum in Lorentz-correction using Bragg's law) for PEKK(I) crystallized via solvent-induced crystallization with and without further annealing

Annealing temperature (°C)	Long period without further annealing (nm)	Long period with further annealing (nm)
250	11.9	11.4
230	11.9	9.6
210	11.9	9.3



Figure 5 TEM observations of PEKK(I) crystals obtained via solvent-induced crystallization without further annealing

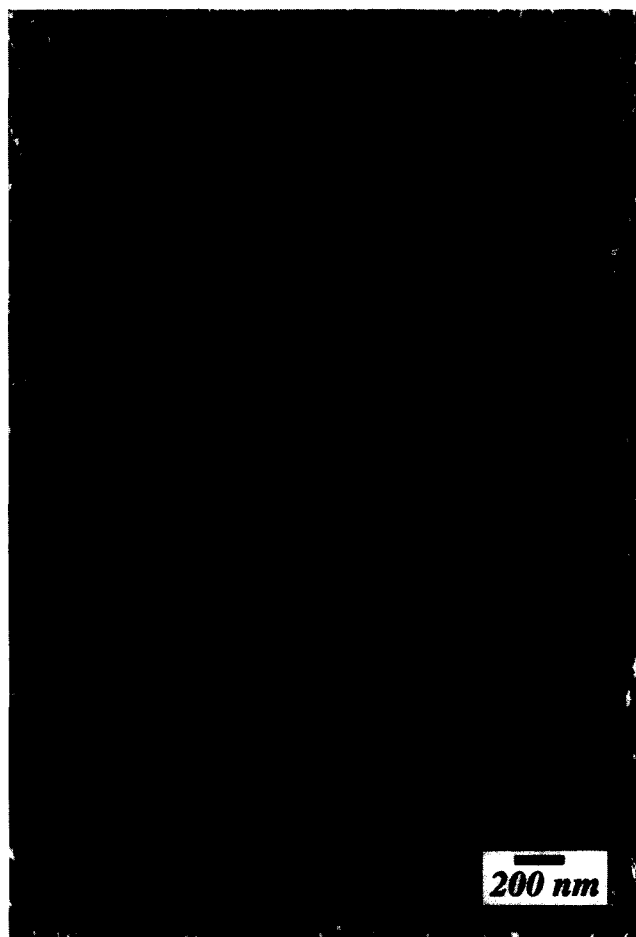


Figure 6 TEM observations of PEKK(I) crystals obtained via solvent-induced crystallization with further annealing at 250°C

separation distance between the lamellar crystals decreases slightly (Figure 6). We suggest that this is attributed to the random arrangement of the lamellar array, which is similar to TEM observations of PEEK¹⁹, and deviates from the edge-on growth of the thin film

samples (see below for detailed explanation). This can be supported by an ED pattern taken from the structure of Figure 5 with an isotropic diffraction ring (see Figure 5).

The results of long period measurements by SAXS experiments for PEKK(I) crystallized via solvent-induced crystallization with and without further annealing are listed in Table 2. The long period decreases after further annealing. This observation is consistent with the mechanism of the growth of subsidiary lamellae. Furthermore, with increasing annealing temperature the values of the long period increase. This may be an indication that the second stage of crystallization to form the subsidiary lamellae and/or reorganization in the previously formed lamellae occur simultaneously during annealing.

Image formation of shadowing in TEM

Shadowing is used to enhance specimen contrast by

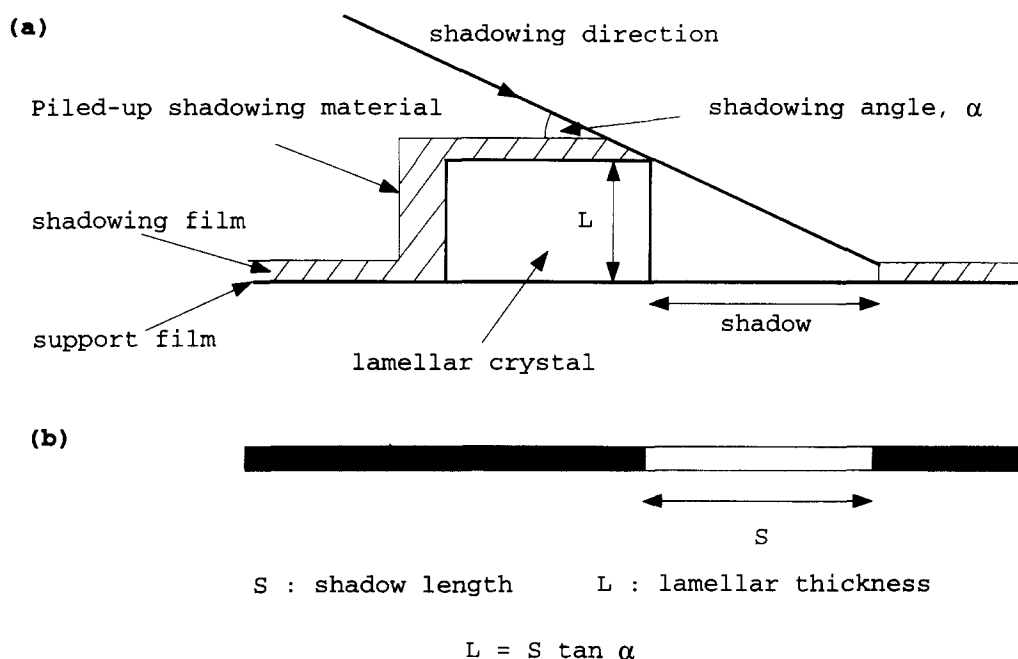


Figure 7 Schematic diagram of a shadowed flat-on growth of lamellar crystals (a) and their morphological texture in TEM (b)

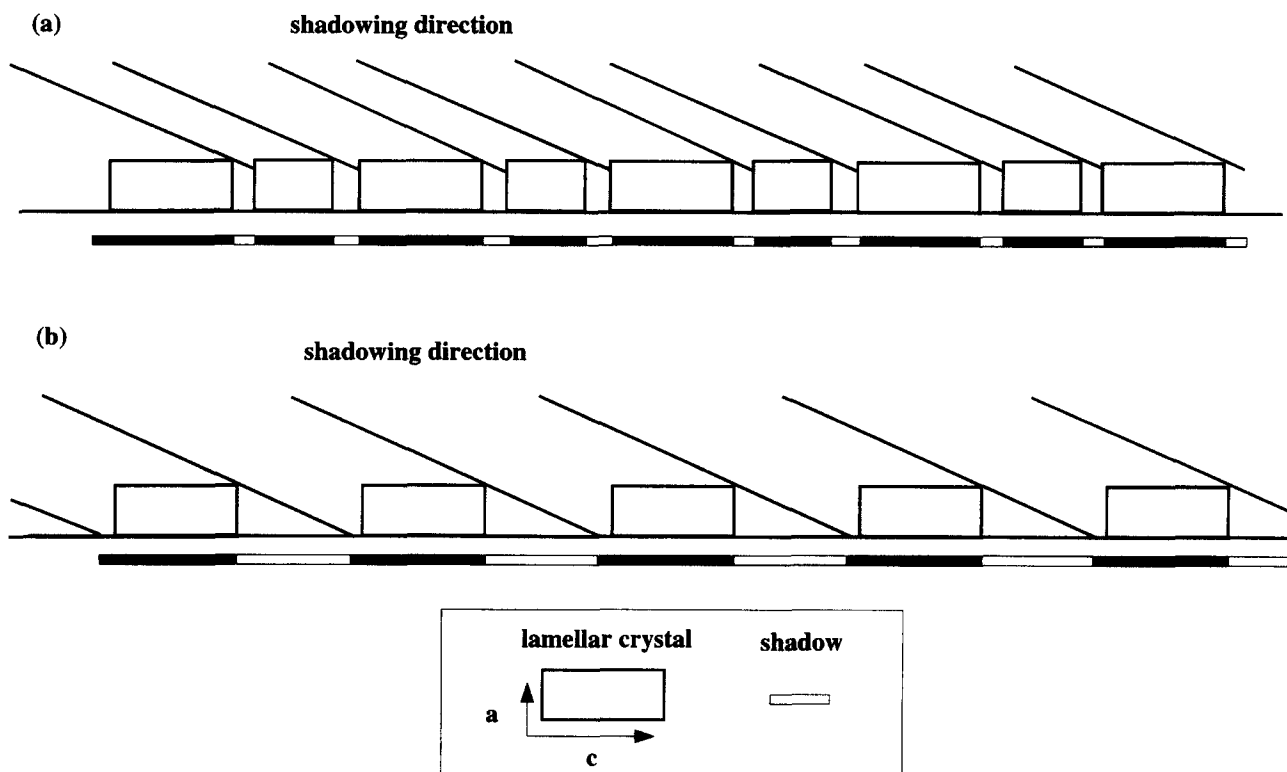


Figure 8 Schematic diagram of a shadowed image for edge-on morphology: PEKK(I) crystallized at 230°C for 2 h from the melt (a) before and (b) after partial melting

increasing electron scattering²⁰. The application of a heavy metal in front of raised areas provides a cover of metal atoms while these atoms are not deposited on the other side. Shadowing at a known angle, generally in a range 20–45°, is useful for measurements of layer heights or sizes. The morphological texture of shadowing in TEM is strongly dependent upon the topography of the sample surface. Based on image analysis of the crystalline morphology, an interpretation about the morphological observations in the melt crystallized PEKK(I) and solvent-induced crystallization may be provided.

Figure 7a schematically shows the result of shadowing on a flat-on lamellar crystal. The area of shadowing metal scatters the majority of the incident electrons while the non-shadowed area allows the electron beam to pass through and expose the film negative. Therefore, a strong contrast of image can be observed (Figure 7b). The lamellar thickness can be calculated based on the length of shadowing and the shadowing angle. For PEKK(I) thin films completely crystallized at above 210°C from the melt, the edge-on growth for lamellar crystals is preferred and the coupled lamellar crystal morphology

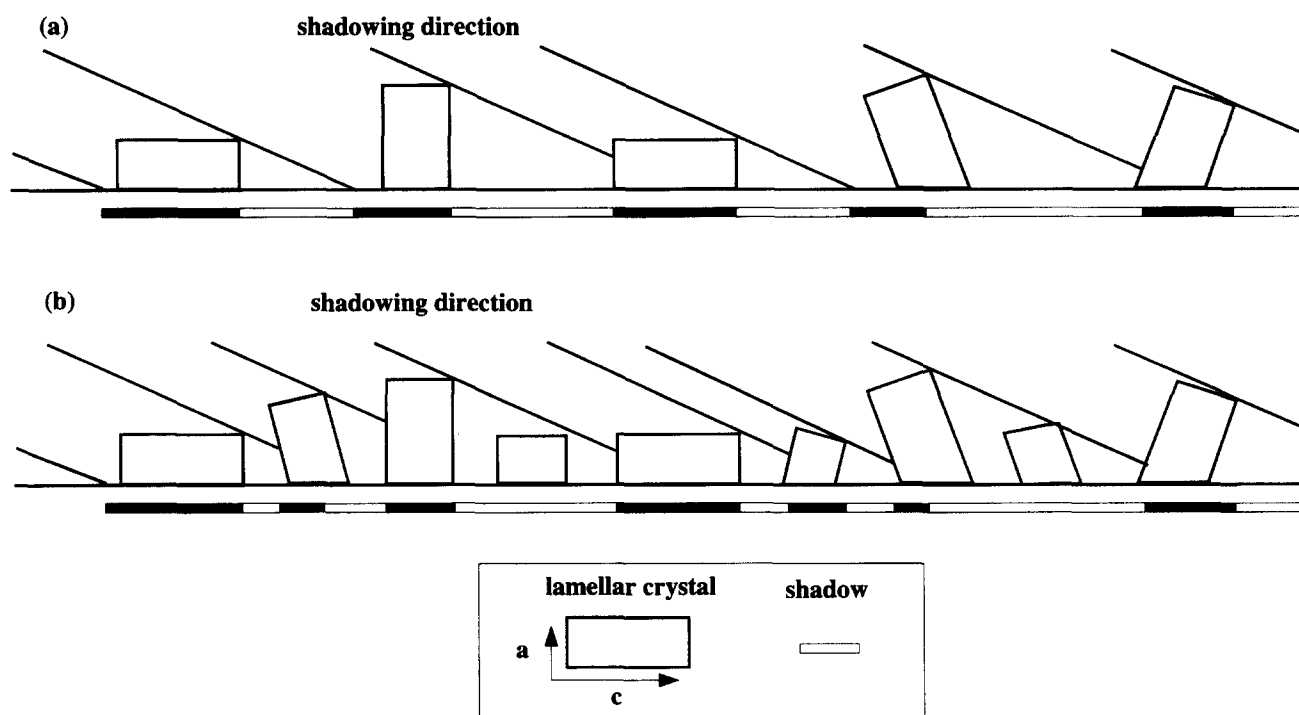


Figure 9 Schematic diagram of a shadowed image for random oriented lamellar morphology: PEKK(I) crystallized via solvent-induced crystallization (a) without and (b) with further annealing

is observed. A possible lamellar arrangement for this morphology may be proposed, as shown in *Figure 8a*. In this case, the length of shadow is dependent upon the separation distance between lamellae and the thickness of the lateral growth (height along the a -axis) instead of lamellar thickness. Note that even in the edge-on lamellar crystal morphology observations, the separation distance observed by TEM deviates somewhat from the long periods determined from the SAXS results. The thinner lamellae only form in those locations where the separation distances and chain mobility allow the growth of these lamellae. In this case the different lamellar thicknesses may not be easily identified. However, a distinguishable morphological texture can be seen, since a larger separation between lamellae can be recognized after partial melting (*Figure 8b*). For PEKK(I) thin films crystallized via solvent-induced crystallization, a random arrangement of the lamellae is found as illustrated in *Figure 9a*, and a non-uniform shadowed image is thus observed through TEM. Although the secondary process for the growth of subsidiary lamellae occurs after further annealing, the observed morphological texture may only exhibit a significant change in the density of lamellar crystals, as illustrated in *Figure 9b*.

Under the assumption that *Figure 8* is a true description of the PEKK(I) crystal morphology shown in *Figures 2* and *3*, it is possible to further study intensity changes in these figures which result from the shadowing procedure. One-dimensional distributions of shadowed areas for the edge-on lamellar crystals change from around 14 nm before the partial melting to 16 nm after the partial melting. Note that the shadowing size is not exactly the same as the lamellar thickness depending upon the shadowing angle and the spacing between lamellae (see *Figure 8*). The question is whether the lamellar crystal morphology observed in thin films may also be different from the corresponding bulk samples.

However, no significant difference in the crystalline morphology in PEEK¹⁹ and PEKKs have been found¹⁸. From this study, both bulk and thin film thermal behaviours are the same. Their bulk long spacing data obtained from SAXS and shading intensity data deduced from the thin film TEM observations also seem to correspond to each other. Further investigation is necessary to systematically explore this issue.

CONCLUSION

We have observed coupled lamellar crystal morphology in the edge-on orientation after isothermal crystallization of thin PEKK(I) films from the melt (above 210°C). The coupled lamellar morphology disappears after partial melting occurs by heating the sample to a temperature above the low endothermic peak. This has been associated with the double endothermic behaviour seen in d.s.c. observations and supported by SAXS observations. In solvent-induced crystallization, the double endothermic behaviour can only be found after further annealing occurs. This accompanies a development of subsidiary lamellae identified by TEM and SAXS. We suggest that in PEKK(I) thin film samples, different components of the morphology with different thermodynamic stabilities form in two stages of crystallization although reorganization does occur during the heating of these isothermally crystallized PEKK(I) samples.

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