On crystallization phenomena in PEEK*

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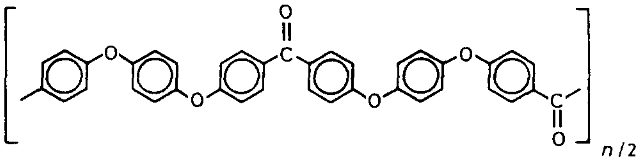
The crystallization and lamellar morphology of PEEK have been investigated by thermal analysis and electron microscopy following permanganic etching. It is shown that the two peaks in typical melting endotherms (of samples which have been crystallized either from the melt or by heating from the glassy state) represent different components of the morphology, formed in two stages of crystallization. The earlier stage is represented by a broad upper melting peak; the lower melting peak develops later. In crystallization from the glass at higher values of T_a, the lower peak represents crystallites which have been reorganized at T_a but which originated from the lower part of the primary endotherm extending below T_a. Additional crystallinity may also develop from a portion of the rubbery phase which did not crystallize initially. In crystallization from the melt at T_c, the first product shows a broad melting endotherm extending down to T_c. After a time, the secondary peak develops; it lies just above T_c, and thus represents crystallites only just stable at T_c. Electron microscopy shows that spherulites of PEEK are constructed from a framework of branching and splaying individual dominant lamellae with subsequent infilling. The dominant and other primary lamellae melt in the upper peak while material melting in the lower peak lies between them. Internal evidence suggests that this correlation of melting point and location within the spherulite architecture is an inherent function of that location, reflecting changing constraints in the sequence of crystal growth, rather than fractional crystallization due to variations in molecular properties. Accordingly, the two melting peaks would be a consequence of spherulitic growth which would be most prominent when later crystallization is difficult to achieve, i.e. in polymers of low crystallinity.

(Keywords: crystallization; PEEK; morphology; thermal analysis; electron microscopy)

INTRODUCTION

The properties of materials depend on their microstructures, especially in semi-crystalline polymers where a complex textural organization intervenes between the long chain molecules and the properties of a macroscopic sample. A modern view of these materials, based on accumulated studies over the last 30 years, is that the evidence supports common microstructural themes stemming from the long chain nature of the molecules with individual variations according to the specific chain structures. Nevertheless the majority of the original evidence is of only one polymer, namely polyethylene, the archetypal flexible linear chain. The behaviour of other polymers has generally been interpreted by comparison with the understanding first established for polyethylene. In PEEK (*Scheme 1*), acronym for poly(aryl-ether-ether-ketone), we have by contrast a polymer with a stiffer chain and a higher melting point, which typically develops only modest crystallinity (around 30%), only a third or so of that of polyethylene. In investigations over the last 3 years, we have studied PEEK from the point of view of morphology (developing a means of observing its representative lamellar morphologies[1]) and of thermal analysis. Experiments using the latter technique have led us to reconsider the interpretation of melting endotherms which had previously been presented[2] in a manner analogous to polyethylene, and thence to the conclusion that the presence of two peaks for isothermally crystallized PEEK is a consequence of two physical locations within the spherulitic texture of the polymer[3]. Confirmatory studies using permanganic etching have identified these as comprising, respectively, higher-melting primary lamellae and lower melting lamellae in between. The association of two melting peaks neither with chemical, nor with molecular weight differences, but rather with morphological siting, is an important new principle for the formation and properties of semi-crystalline polymers.



Scheme 1 Formula of PEEK showing two repeat units

EXPERIMENTAL

Source of materials

PEEK was supplied by Dr D. J. Blundell (ICI plc, Petrochemical and Plastics Division) in the form of glassy sheets, with a thickness of 1 mm. The molecular mass of this PEEK is not known exactly, but the mass average is known to be of the order of 4×10^4.

Thermal analysis

Differential scanning calorimetry (d.s.c.) was carried

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out for most samples in a Perkin–Elmer DSC-1B instrument, but some experiments, particularly those requiring thin samples for fast scan rates, were repeated later using the more sensitive DSC-2C. In general, about 10 mg samples of the sheet PEEK were used. All thermal experiments in the d.s.c. were done in a nitrogen atmosphere to prevent oxidation of the specimen. A 16 K min^{-1} scan rate was selected in all experiments unless otherwise indicated. Melting points were calibrated by scanning standard melting point substances, usually lead or bismuth, at the same rate. This allowed two corrections to the ordinate, both of which are essential for detailed comparisons to be made. One of these is the correction for thermal lag in the differential control loop, obtained from the leading edge slope of the indium or bismuth endotherm. The other, of particular relevance when comparing different scan rates, is for thermal lag in the average control loop, which adds directly to any error in the instrumental calibration. This is simply obtained from the position of the standard melting peak at the given scan rate. Both of these are described in the appropriate operation manuals.

The heat of fusion ΔH_{exp} was obtained by measuring the area under each melting curve, and making a proportional correction for the instrumental parameters such as scan rate, sensitivity and chart speed. Baselines were determined on the DSC-2C by running an empty can, giving a curve which could be subtracted digitally from the sample curve. From the DSC-1B only graphical output was obtainable, and so a baseline was drawn using a cubic spline tangent to the endotherm at points immediately prior to and after melting, following an appropriate geometrical construction. This is a compromise between the two methods of baseline construction described by Blundell *et al.*[4], and in addition allows for instrumental baseline curvature up to the third order. Although not totally rigorous thermodynamically it gives good systematic comparisons between different samples in a sequence of experiments.

The crystallinity of a sample was obtained from the endotherm, the fractional crystallinity χ_c being calculated from the equation:

$$\chi_c = \Delta H_{\mathrm{exp}} / \Delta H \qquad (1)$$

where ΔH is the heat of fusion of fully crystalline PEEK[2], with a value of 130 J g^{-1}.

Electron microscopy

The internal morphology of PEEK was revealed by etching with a solution of potassium permanganate 2% w/v in a mixture of 4 volumes of orthophosphoric acid and 1 volume of water[1]. After etching, the samples were washed with several changes of distilled water and allowed to dry. Most often, two-stage replicas were used, a first stage Triafol replica being shadowed with platinum/palladium alloy and backed with carbon, then the Triafol extracted with acetone. (For *Figure 5*, where better resolution was essential, a more elaborate direct replication technique was used.) All the electron microscopy reported in this work was carried out on a Philips 301 transmission instrument.

Crystallization and annealing procedures

PEEK can be crystallized either by cooling from the melt or heating from the glass (annealing). Both methods have been followed here, together with a third, intermediate, variant (self-seeding) which is used to control nucleation.

Melt-crystallization. PEEK was melted in the d.s.c. by heating the sample from room temperature to 400°C. After 1 min at this melt temperature the d.s.c. was set to the chosen crystallization temperature (280, 300, 310, 320 or 330°C) which the sample reached in approximately 30 s. The samples were held at the crystallization temperatures for selected times before being allowed to cool quickly to 100°C. After cooling the sample was remelted and its endotherm recorded, sometimes in the DSC-2C at a series of different scanning rates (1.25, 5, 20 or 80 K min^{-1}), but more often in the DSC-1B at 16 K min^{-1}. However, in some experiments the specimen was not allowed to cool: it was reheated directly from the crystallization temperature up to 380°C at 16 K min^{-1}.

Annealing. Samples of glassy PEEK were heated in the d.s.c. from room temperature to the chosen annealing temperatures ($T_a = 300$, 310, 320, 330 and 340°C). The samples were maintained at this temperature for selected times before being cooled quickly to 100°C. Samples for electron microscopy were removed from the d.s.c. after cooling to 100°C, but to measure the endotherms other samples were reheated directly from T_a.

Self-seeding. Glassy specimens of PEEK were heated at 16 K min^{-1} to a suitable nucleation temperature, above 340°C. After holding for 1 min they were cooled to 330°C and held at that temperature for 2 h (unless stated otherwise) before being cooled quickly. After cooling the specimens were removed from the d.s.c. for electron microscopy, or remelted to obtain the endotherm.

RESULTS AND DISCUSSION

Melting endotherms of PEEK crystallized from the melt

The first melting endotherms of PEEK were reported by Blundell and Osborn[2]. These have the character of our own results shown in *Figure 1*. Material crystallized isothermally from the melt at temperature T_c generally shows a small peak 10–15 K above T_c and a broad higher peak with a maximum typically in the range 330–340°C. Material heated from the glass exhibits a sharp exothermic peak due to crystallization at around 180°C and a subsequent broad melting peak with a maximum near 330°C. However, if the sample is taken from the glass and held at a temperature T_a between these two peaks, then cooled and reheated, a small endothermic peak about 10 K above T_a results. Blundell and Osborn identified, in both procedures, the peaks just above T_c or T_a with the melting of lamellae crystallized at these temperatures. The higher peaks they interpreted as due to the melting of lamellae which had reorganized during the scanning in the calorimeter. This is the same interpretation as given for poly(ethylene terephthalate)[5,6], in terms of a process first shown long ago to occur in polyethylene.

The reason why reorganization is possible during a rising temperature scan is that polymers crystallize as metastable lamellae, which have their melting points depressed because of their large surface/volume ratios and the high surface free enthalpies of their basal (fold)

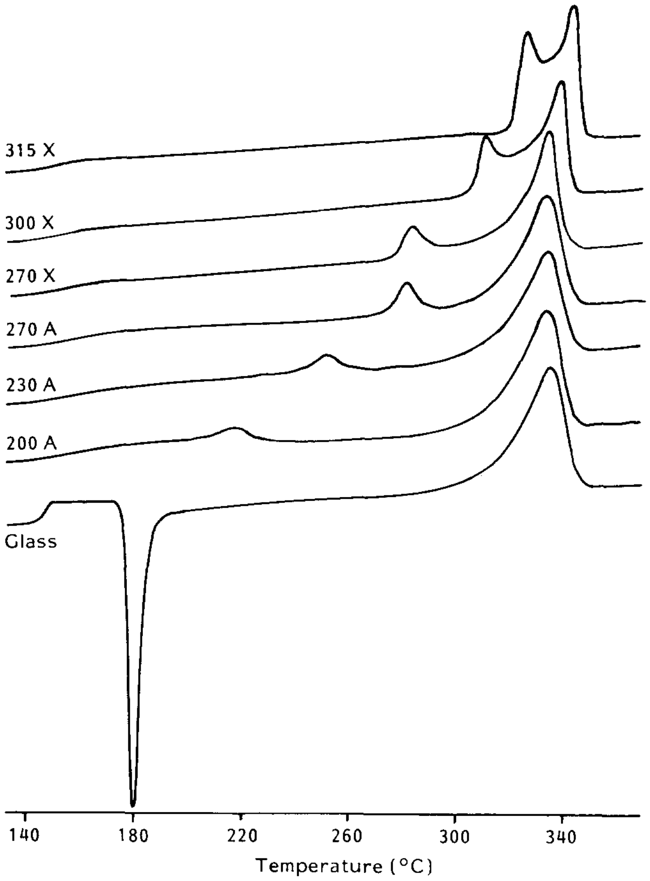

Figure 1 Melting endotherms of PEEK specimens: (200A, 230A, 270A) annealed (A) from the glass for 1 h at the indicated temperature; (270X, 300X, 315X) crystallized (X) from the melt for 1 h at 270 and 300°C, and 4 h at 315°C. All scanned at 20 K min^{-1}

surfaces. In principle it is possible to reduce the chemical potential of the system by increasing the thickness of the lamellae. A common means of achieving this is partly to melt then to recrystallize a sample, thereby transferring material from the lower towards the higher temperatures in the subsequent endotherm. Of course it is also necessary that sufficient time is available for recrystallization, but the kinetics are enhanced by the presence of unmolten nuclei. Recrystallization can also involve fractionation by molecular length[7] and, as demonstrated for linear-low density polyethylenes, on branch content[8,9]. Details have been evaluated in various instances including previous work from this laboratory[11]. Furthermore melting of these other polymers at different scan rates confirms the interpretation of reorganization during scanning by showing that, at the slowest rates there will be 100% reorganization, at the fastest rates none, and in general a double peak indicative of part transformation[12]. In polyethylene there is no doubt that double peaks in the melting endotherm can be an artefact of the measurement technique rather than a characteristic of the original polymer. Equally they can also represent different populations relevant to the history of the sample.

The phenomena shown by PEEK do not support an origin of the two peaks in reorganization during scanning. *Figure 2* and *Table 1* show the results of measuring the melting endotherm of PEEK crystallized from the melt at 310°C, at different scanning rates. The variations in peak size are modest and, even at the highest rate (80 K min^{-1}) show no evidence for a single untransformed melting peak. Reorganization would have to be fast compared with the highest scanning rate to retain the double-peaked character almost undiminished. On the other hand measured crystallization rates above 300°C are relatively slow, occurring on a time scale of minutes or longer (see below). One can reasonably infer, therefore, that the two peaks in the endotherm relate primarily to different initial textural components with no more than modest reorganization.

A direct test of this hypothesis is illustrated in *Figure 3*. Here the same specimen (to minimize uncertainty in the d.s.c. baseline) was crystallized from the melt at 310°C for various times, in two concurrent series. In one series (*Figure 3a*) the sample was cooled from 310 to 200°C prior to rescanning, and in the other (*Figure 3b*) it was scanned directly from T_c without cooling. During the sequence the crystallization exotherm remained reproducible, even after 22 h at 310°C, indicating that no significant degradation of the sample took place. Comparison of the two shows the time sequence of isothermal crystallization and also identifies populations formed on cooling. In detail, the results are as follows:

1 min. No appreciable isothermal crystallization has taken place. On the right all that is observed is an instrumental transient followed by uninterrupted baseline, so that on the left the peak must be due to material crystallized on cooling;

6 min. The primary (upper melting) population is a little over half developed, showing, on the right, a partly developed peak. One expects, therefore, to see, on the left, a combination of two peaks. The single broad endotherm observed is, indeed, consistent with a combination of the

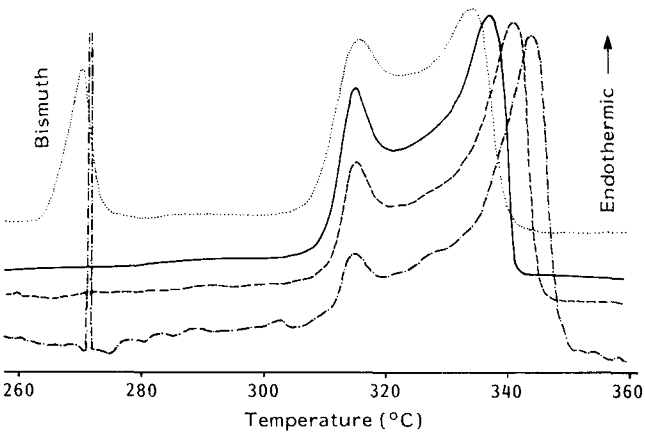

Figure 2 Melting endotherms of PEEK crystallized from the melt for 1 h at 310°C. Scanned at: –·–·–, 1.25; ---, 5; ———, 20; ·····, 80 K min^{-1}. Also shown for the fastest and slowest scan rates are the exotherms from the accompanying piece of bismuth, to illustrate the instrumental effect on the shape of the curve. Note that the endotherms are arranged so that the maxima of the final peaks are correctly placed with respect to temperature, after correction for instrumental factors

Table 1 Maxima of final melting peaks at different scan rates for PEEK crystallized at different temperatures

Scan rate (K min^{-1})	Crystallization temperature (°C)		
	200	310	320
80	326.3	333.4	341.1
20	332.4	336.7	342.9
5	337.5	340.7	343.9

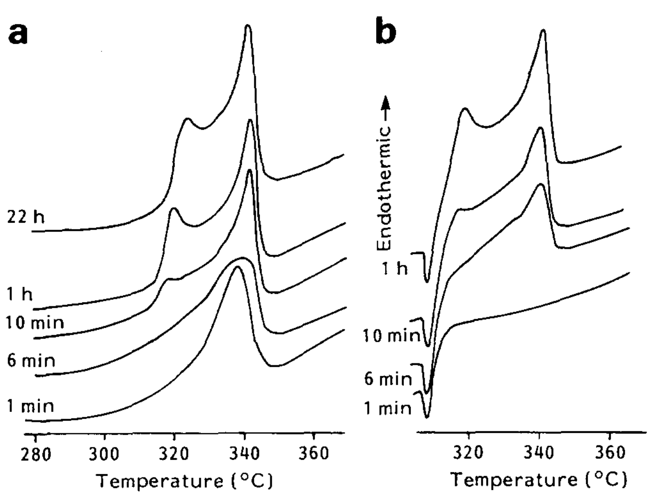

Figure 3 Melting endotherms (16 K min^{-1}) of PEEK crystallized from the melt at 310°C for different times. (a) Cooled to 200°C and rescanned; (b) scanned directly from the crystallization temperature

trace for 1 min (below) and the upper peak for 10 min (above);

10 min. Endotherms in both diagrams are now substantially the same. The primary population is completely developed, coincident with the end of the crystallization exotherm observed in other experiments. It shows a melting maximum which will remain largely invariant in shape and position on prolonged treatment. Now the secondary population is beginning to form, with a small peak at ≈318°C just becoming apparent;

1 h. The secondary population is now well developed, giving a prominent peak at 320°C;

22 h. The secondary population has developed somewhat giving a higher melting point at 324°C.

Such data show simply and clearly that the crystallites which form first are higher melting than the subsequent ones. The upper peak cannot have formed from the lower, and the two melting peaks therefore represent different components of the morphology. As a corollary we note that the melting points of samples cover a broad range, but with maxima as much as 150 K above their T_c, very much more than is the case in polyethylene. The above conclusion has been confirmed and extended by examination of the interior morphology of the sample using electron microscopy following permanganic etching.

Electron microscopy

PEEK shows a pattern of spherulitic crystallization similar to that found extensively in other polymers, namely a framework of dominant lamellae followed by infilling growth[13]. This pattern is most easily recognized if one examines the early stages of growth, i.e. with simple objects grown slowly at high temperatures. Two stages of growth are shown in *Figure 4*; the objects are easily distinguishable from a surrounding matrix crystallized very rapidly on quenching. The very earliest, in *Figures 4a* and *b* (330°C, 1 h) are lathlike crystals seen in two projections. That in *Figure 4a* is seen in plan but is inferred to be not quite flat-on, because one end, towards the top of the figure, appears to have been eaten away during etching. The middle of the crystal, forming the upper part of the object as seen, has a characteristic internal texture along the length of the lath, like that found in similar lath-like objects crystallized from solution by Lovinger[14–16]. This reinforces the parallelism between lamellae grown from solution and from the melt, whose comparison permanganic etching has facilitated. The bottom end of the object appears to have divided into two during growth at T_c, with further splaying in the bottom 100 nm formed on quenching. In *Figure 4b* the full length of a similar object, lying nearly sideways-on, is displayed. A more advanced stage of growth is seen in the immature spherulites in *Figure 4c* (310°C, 5 min). The complete objects are in the shape of two flat fans radiating from a common centre. In the top right quadrant of the picture, one fan is seen; the other half of the object is missing as it did not lie exactly in the etched surface. In the fan shown one has a clear view of the first-formed dominant lamellae interleaved near their extremities with quenched melt (arrowed), but further in by subsidiary growth. At this early stage the subsidiary growth must contribute to the ramp-like rise of the primary peak in the endotherm, since no secondary peak is yet observable in specimens crystallized for such a short time. In the

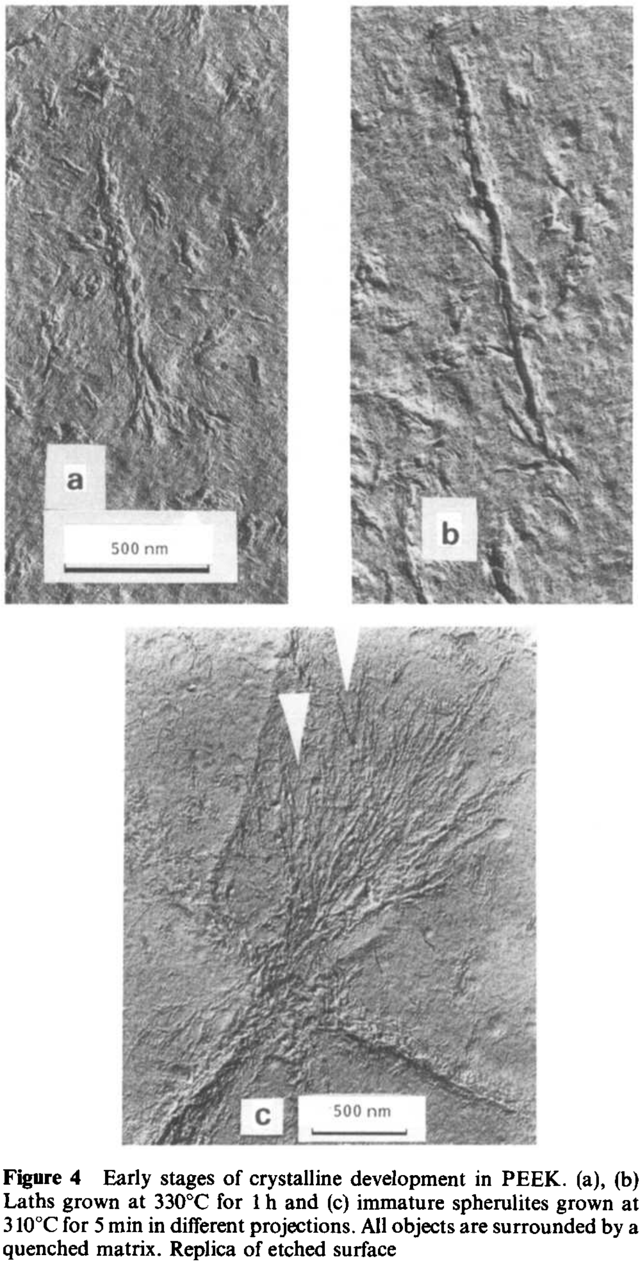

Figure 4 Early stages of crystalline development in PEEK. (a), (b) Laths grown at 330°C for 1 h and (c) immature spherulites grown at 310°C for 5 min in different projections. All objects are surrounded by a quenched matrix. Replica of etched surface

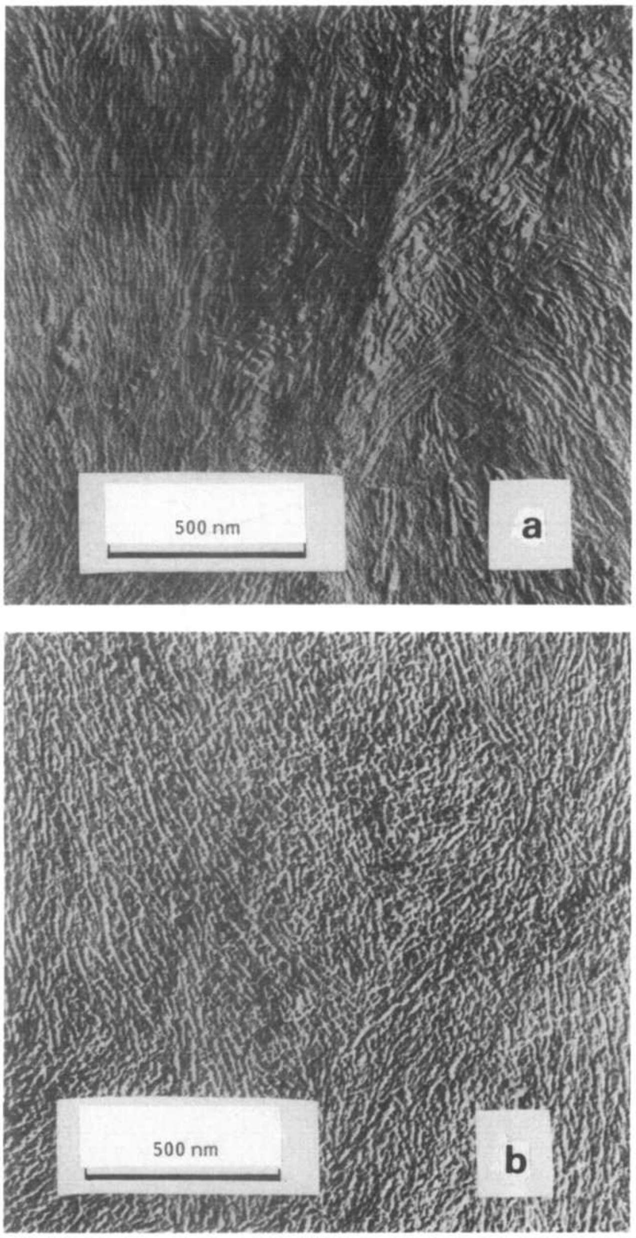

Figure 5 Surfaces of PEEK crystallized at 330°C for 17 h. (a) Etched as crystallized, (b) etched after melting out and quenching the lower-melting population in the d.s.c.

bottom right quadrant part of another object is seen in a different projection, showing how nearly two-dimensional these early objects are. In this they resemble the morphology exhibited by isotactic polypropylene grown at 160°C[31].

In contrast to the developing habits of *Figure 4*, we show in *Figure 5a* detail of a sample fully crystallized at 330°C, namely radiating arrays of rather ill-formed laths. The region shown is the central part of a large spherulite, whose outer boundaries are well beyond the region displayed. The melting endotherm of this sample contains two peaks as in *Figure 6a*. If one subsequently heats the sample to a temperature between these two peaks, namely 350°C, then quenches it, the lower melting peak moves to lower temperatures (*Figure 6b*) and the etched sample now appears as in *Figure 5b*. In both pictures we see an array of what we shall term *primary* lamellae; we use this term to refer to lamellae contributing to the upper melting peak, rather than the term *dominant* which we frequently use when describing textures in real space, because the experiment makes no observable distinction between dominant and subsidiary among the lamellae left standing proud in *Figure 5b*. In *Figures 5a* and *b* the primary lamellae have the same separation (giving the same scattering angle in a low-angle laser light-scattering experiment). However after its melting the intervening material has recrystallized to form much thinner lamellae than before, so it is much more readily etched away, in a similar manner to that established in detail for polyethylene[28,29]. The unmelted lamellae therefore now stand out much more in the etched surface. This is a demonstration in real space that material comprising the lower melting peak lies between primary lamellae. However, in other polymers, isothermal crystallization of the same phase has not been shown to lead to two melting peaks. Most notably in polyethylenes, fractionation occurs, which on quenching can lead to lower melting peak(s) of different molecular constitution[7,9,11]. For PEEK, the identification of two partly concurrent crystallization processes, *linked to different physical locations in the microstructure*, represents an additional aspect of polymeric behaviour.

Crystallization from the glass, and annealing

Further evidence is provided by the behaviour of PEEK crystallized by heating the glass. *Figure 7* (see also *Table 1*) illustrates endotherms recorded at different scanning rates for a sample crystallized from the glass and annealed at 200°C for 1 h. The changes parallel those for melt crystallized PEEK shown in *Figure 2*, with the melting point of the upper peak decreasing at faster rates but a minimal decrease in the size of the small low-melting peak at 5 K min^{-1} as compared with 80 K min^{-1}. We conclude that this again precludes reorganization of the low-melting peak as being the origin of the upper peak, but the material melting within the upper peak is itself capable of modest reorganization at the slower heating rates.

The origin of the low melting peak will be considered presently, but first there is detailed evidence as to how material giving the broad (upper) melting peak can be reorganized by controlled annealing procedures. The behaviour to be described is similar to that of linear-low

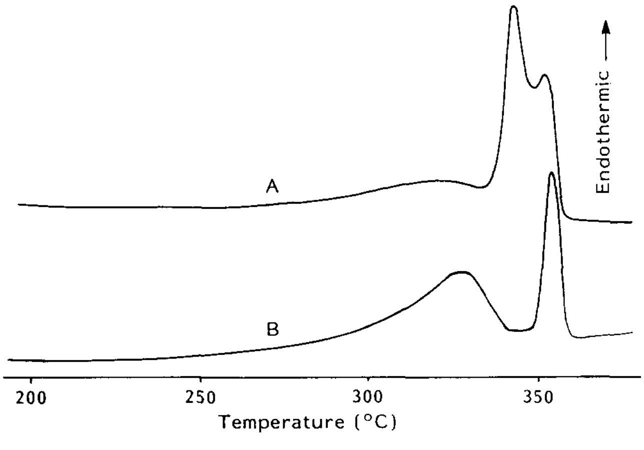

Figure 6 Melting endotherms (at 20 K min^{-1}) of PEEK corresponding to the samples in *Figures 5a* and *b*. A, Before; B, after partial remelt

Table 2 Melting behaviour of annealed PEEK

Annealing temperature and time (min)	Peak melting temperature			ΔH_f (J g^{-1})		Crystallinity (%)
		Isothermal				
	Cooled	Lower	Higher	Cooled	Isothermal	
300°C 1	–[a]	306.5	333.5	3	36	30
10	–[a]	309.2	333.4	10	46	43
310°C 0	–[a]	315.5	334.3	5	38	32
10	–[a]	318.5	334.6	5	44	37
320°C 1	–[a]	326.5	333.6	11	32	33
10	–[a]	327.2	334.4	19	41	46
100	–[a]	328.9	shoulder	20	46	50
1020	–[a]	–	333.6	28	50	60
330°C 1	–[a]	–	335.0	27	18	35
10	–[a]	–	335.5	32	29	47
340°C 1	334.6	–	344.5	46	2	37
10	333.6	–	346.7	49	4	41
100	331.5	–	348	42	12	42
1020	327.3	–	349.7	41	18	45

[a] Too broad for a precise temperature to be given

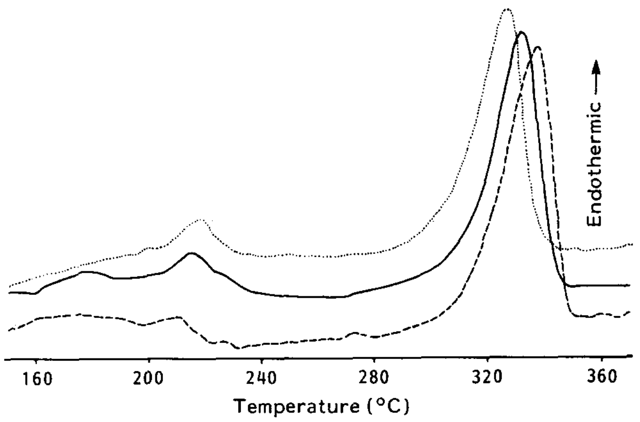

Figure 7 Melting endotherms of PEEK crystallized from the glass for 1 h at 200°C. Scanned at: – – –, 5; ———, 20; · · · · ·, 80 K min^{-1}

density polyethylenes crystallized from the melt where the texture laid down during crystallization from the melt is progressively adjusted by annealing at increasing temperatures[11]. This provides evidence that the upper melting peak represents the structure established when PEEK crystallizes from the glassy (more strictly, the rubbery) state.

Experience with linear-low density polyethylene and other polymers leads to the expectation that annealing at progressively higher temperatures within the original broad upper melting peak will give the following behaviour[30]. Firstly, material which melts below the annealing temperature T_a will recrystallize at T_a to a higher lamellar thickness, and now melt a little above T_a. At annealing temperatures of 320°C and below this is identified for PEEK by the appearance of a small peak at the beginning of the modified endotherm (*Figure 8*, see also *Table 2*). The shape of this peak is quite similar to the secondary peak found in melt-crystallized material, but it develops much more rapidly. For example, at $T_a = 310$°C it is already apparent in a 'zero time' annealed sample which has been cooled instantly on reaching T_a (*Figure 9*), and has thus spent only a few seconds in the vicinity of the treatment temperature; its subsequent development is also more rapid.

Secondly, at higher T_a more material will have been melted from the original broad range but the kinetics of recrystallization will be slowed because of the higher temperature. It is expected, therefore, that at sufficiently high T_a some material will be unable to recrystallize at T_a in the time available, but will do so on cooling. This, in turn, would be recognized by the appearance of a broad melting region below T_a in the melting endotherm of the annealed polymer. This is a prominent effect in polyethylene[11,30] but is slight in our PEEK samples, being first detectable (*Figure 8*) in the curve for $T_a = 330$°C. One can tentatively conclude from this that the molecules of this PEEK sample are relatively homogeneous in their ability to crystallize, with only a small amount of low mass components evident. This reinforces the interpretation of different melting points as deriving from textural rather than molecular causes.

The merging of the reorganized low peak with the (more perfected) remnant of the original is well seen, both as an effect of temperature in *Figure 8* (330°C, 10 min), and also of time in *Figure 10* (320°C, 17 h), where the two constituents were clearly present at the start, but eventually are no longer resolved. On heating further to $T_a = 340$°C one sees (*Figure 8*) a sharp high temperature peak on the high side of a broad curve resembling that in the original trace. This phenomenon, too, is familiar from polyethylene[11,30]. The narrow high peak (which increases in size and melting point with time of annealing) is due to self-seeded polymer melted and recrystallized at 340°C. The remainder has recrystallized on cooling over a spectrum of conditions. At this stage electron microscopy can again furnish useful information.

Morphology of PEEK after annealing and recrystallization

Prior to 340°C, the rises in melting point produced by annealing have little obvious effect on the appearance of etched PEEK. The gross morphology remains the same, consisting of small spherulites with tortuous lamellae, for example in a specimen annealed for 17 h at 330°C (*Figure 11a*). It has previously been shown[1] that this appearance is typical of PEEK crystallized from the glass, in contrast to that from the melt. An extreme case of such curved lamellae is found in PEEK slowly crystallized from the glass at 163.5°C (*Figure 12*). Annealing below 340°C produces small-scale local changes within this structure but does not disrupt the structure itself. In the vicinity of 340°C, the spherulitic structure is completely broken

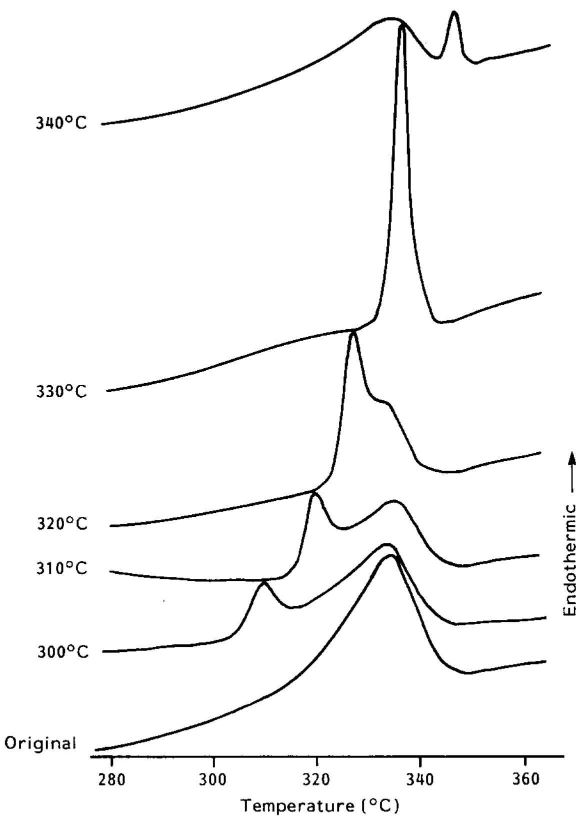

Figure 8 Melting endotherms (16 K min^{-1}) of originally glassy PEEK after annealing for 10 min at different temperatures in the range 300–340°C

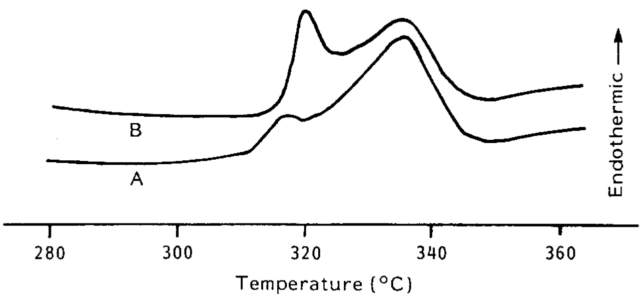

Figure 9 Melting endotherms (16 K min^{-1}) of originally glassy PEEK annealed for (A) zero time and (B) 10 min at 310°C

down; now one sees a rather featureless texture as in the specimen annealed at 340°C for 17 h (*Figure 11b*), though its precise appearance depends on whether one melts to form a dense array of isolated nuclei and quenches immediately or leaves the specimen for a long time to recrystallize at T_a. Above 340°C, annealing reduces the number of nuclei so that, after cooling, individual spherulites are again visible, but this time composed of the well ordered lamellae characteristic of melt-crystallized material. The spherulite size increases dramatically with increasing T_a, but at 350°C self-seeding is still in evidence, since the spherulites are of the order of 1 μm in diameter as opposed to several microns attainable if the material is completely melted.

Development of the low-melting peak on annealing

It has already been shown that the lower-melting peak just above T_a develops with the time of annealing the originally glassy PEEK (*Figures 9* and *10*). *Figure 13a* shows that it does not occur if the scanning is stopped at $T_a = 200°C$ and the sample is immediately cooled and rescanned. In the subsequent d.s.c. trace of the now crystalline PEEK one sees a broad low peak extending between ≈150°C and 210°C. Annealing at 200°C for 15 min produces a small crest centred at 213°C which extends the upper limit of this peak to ≈225°C (*Figure 13b*).

The significance of this broad peak, as observed after an 'instant' anneal at 200°C is that annealing has improved the ordering within the sample. We may infer this by a thermodynamic argument. Above and beyond 215°C the endotherm is indistinguishable from that of unannealed glassy PEEK which has crystallized during heating giving the ≈180°C exotherm of *Figure 1*. Here these two samples are equally separated from the thermodynamic standard state of the melt, i.e. they have the same entropy, enthalpy and Gibbs function. However at lower temperatures the entropy of the annealed sample must be the lower of the two because this sample has to absorb extra heat to reach the condition of equality at 215°C. Because the entropy is the negative derivative of the Gibbs function with respect to temperature, it follows that the annealed sample also has the lower Gibbs function at temperatures up to and somewhat beyond that of the annealing. This is what one would expect because annealing generally provides mobility facilitating the movement to lower free energies.

It also follows that the lowering of entropy for a sample taken to T_a and back will give an equivalent evolution of heat in the attainment of the more ordered state. For a

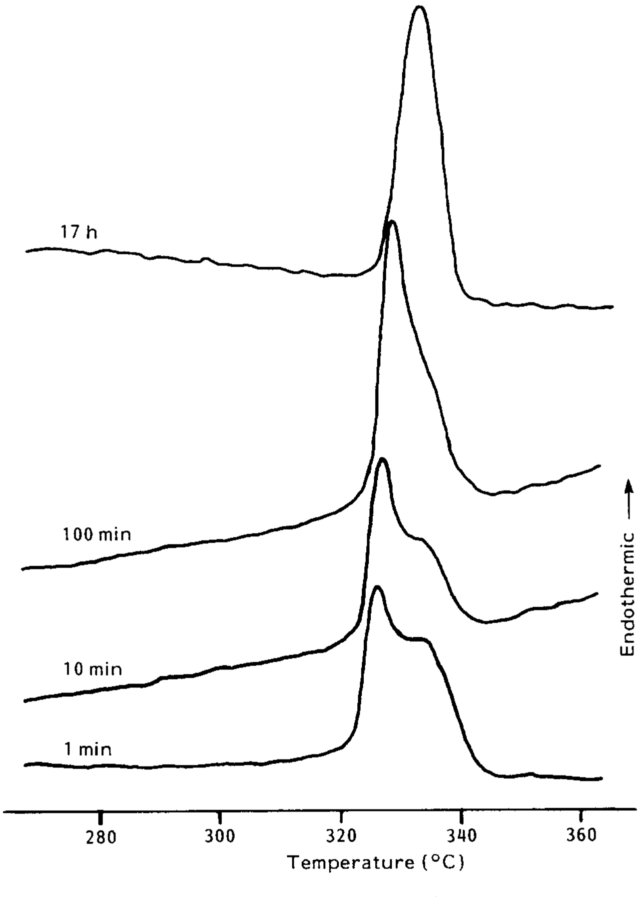

Figure 10 Melting endotherms (16 K min^{-1}) of originally glassy PEEK annealed for different times at 320°C

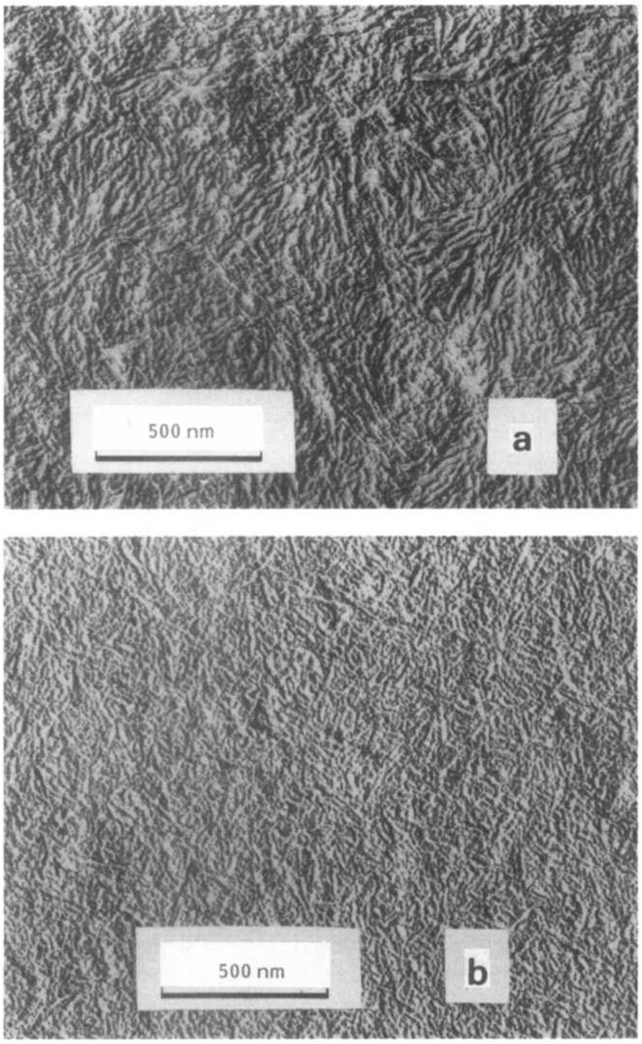

Figure 11 Lamellar textures of glassy PEEK annealed for 17 h at (a) 330°C and (b) at 340°C. Electron micrographs of replicas of etched surfaces

prolonged anneal there are increases in order (the peak in the endotherm just above T_a, *Figure 13b*) which have evidently been produced at temperature. Correspondingly there must be a secondary crystallization process[25] at the annealing temperature which, because the peak is still developing on the time scales used, will extend also to the cooling cycle. By secondary crystallization we do not mean to imply a specific mechanism, merely that it is later than the first or primary crystallization. Nor at this stage do we exclude mechanisms such as solid-state thickening which could enhance ordering although evidence would need to be provided that such additional processes are involved. The phenomena of annealing will naturally include changes in the least stable crystals. It is likely that at T_a *ca.* 200°C the additional crystallinity either develops from a portion of the rubbery phase which failed to crystallize initially, or from improvement of poorly formed crystals; but T_a *ca.* 300°C is well into the rise of the primary melting endotherm, and there local melting and recrystallization must play a major role.

Two lamellar populations

We have seen by etching and microscopy, that in melt-crystallized PEEK primary lamellae have the higher melting points, while lamellae between them give the lower or secondary peak. We have not yet carried out an experiment to ascertain whether this is also the case for PEEK crystallized from the glass but, on the basis of a morphology of splaying lamellae (*Figure 12*), it would seem very likely that the distinction is general.

Plausible reasons for such a dichotomy of lamellae include a phase change or fractional crystallization. However, we have no evidence for the former, while the latter receives no support because of the internal evidence of crystallization; we have already noted the absence of a peak due to material unable to crystallize at the treatment temperature until this attains 330°C (*Figure 8*). In linear low density polyethylene such a peak, due to shorter and more branched molecules, is observed even at low T_a[11,30], so that its very restricted occurrence in PEEK argues against the significant involvement of fractional crystallization in this instance. It thus seems necessary instead to examine possible thermodynamic reasons for the differences in melting point.

The factors which principally determine the melting point of a lamellar crystal are T_m°, the melting point of an infinitely thick crystal, σ_e its fold surface free enthalpy and l, its thickness. It seems very likely, bearing in mind both the great breadth of the melting endotherm of PEEK crystallized from the glass and the similar shapes and peak position for samples crystallized from the melt at all temperatures <315°C, that there is a wide range of environments for crystallites in PEEK. We might, therefore, expect variations in all three quantities cited above. One reason for variation of T_m^0 might be systematic lattice distortion, for which as yet there is no evidence. Another might be ordering, i.e. alignment of chains in the melt, but this is known to raise T_m° in polyethylene because of the associated rise in free enthalpy, whereas we are looking for a reduction.

Conversely, more constrained crystallization should raise σ_e and lower melting points but as the magnitude of σ_e is expected to be mostly the work of chainfolding no large effect would be anticipated. Constrained crystallization reducing crystal thickness seems the most

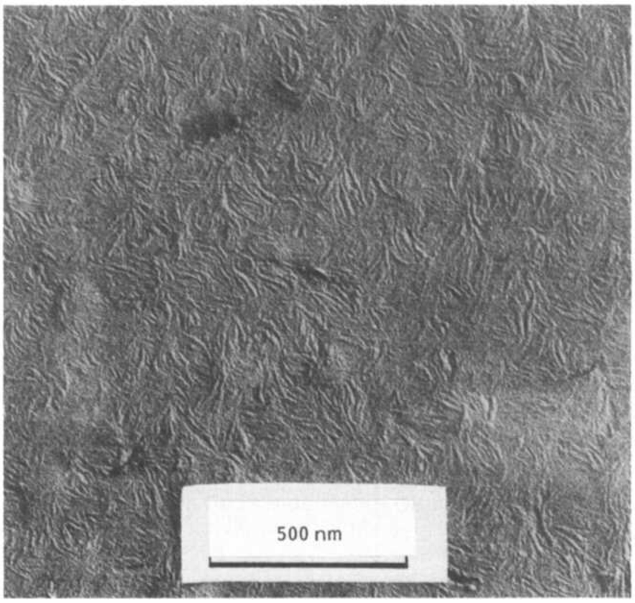

Figure 12 Morphology of PEEK crystallized from the glass at 163.5°C for 15 s. Electron micrograph of replica of etched surface

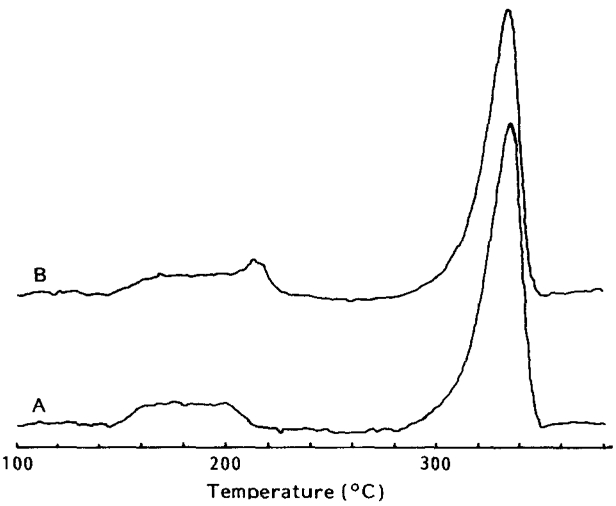

Figure 13 Melting endotherms (20 K min^{-1}) from 100 to 240°C of (A) glassy PEEK, heated to 200°C, then instantly cooled at 80 K min^{-1}; (B) a similar specimen, but held at 200°C for 15 min prior to cooling

likely explanation of the phenomenon. There is a precedent in the crystallization of linear polyethylene[17], with large effects observed for high pressure annealing and crystallization and attributed to reduction in isothermal thickening. Similar, though smaller, effects have been reported at zero and ambient pressures[18]. Experiments to test this explanation using synchrotron radiation as a source for small-angle scattering studies are in hand.

Implications for crystallization and spherulitic growth

The concept of some kind of secondary crystallization is an old one in polymer science[20]. It is usually postulated from the way that Avrami coefficients characteristically fall as melt crystallization proceeds, and envisaged as crystallization in progressively restricted circumstances within and between spherulites. The concept of increasing environmental restriction is well in accord with our observations here. In one view[19], which our findings do not substantiate, it would represent vestigial solidification of polymer rich in poorly crystallizable species, segregated and concentrated between lamellar groups or 'fibres'. Substantial effort has also been spent on small-angle X-ray studies with interpretations offered in terms of lamellar thickening, increases in the thickness of interlamellar regions, or their integrated density deficit[20]. With our combination of thermal analysis and real-space imaging following permanganic etching we can now be more specific.

In PEEK crystallized at 330°C (*Figures 5* and *6*) the primary peak in the endotherm is quite narrow, but it will contain within it contributions from dominant or later-forming primary lamellae. But at lower crystallization temperatures, such as 310°C (*Figures 3* and *4*), the primary peak is broad, extending downwards from the final melting point, and extending to, but truncated at, the crystallization temperature. Here it is quite reasonable to assign the high-melting end to the dominant lamellae, and the lower portion to subsidiary lamellae crystallizing in increasingly restricted circumstances. One observes a slowing of the kinetics and material continuing to crystallize with T_m just above T_c (it cannot crystallize to give $T_m < T_c$) thereby producing a bimodal distribution. In the case of heating from the glass the developing low thermal peak clearly shows (*Figure 13*) secondary crystallization from the rubbery state and possibly reorganization of the lower end of the very broad distribution of lamellar stabilities laid down in the crystallization at ≈180°C. The lower peak developed during melt growth represents the slow establishment of additional crystals, just stable at the crystallization temperature, presumably as the system explores possible routes to stability.

What we have now been able to show with permanganic etching is the spatial location of the low melting material: it lies (*Figures 5a* and *b*) between individual primary lamellae. In this sample we must have all the lower melting material (about half the crystalline component) plus all the non-crystalline interleaved between the primary lamellae giving the spherulite a characteristic internal lamellar texture. This contrasts with the view that lamellar textures in spherulites are a consequence of fractional crystallization with groups of lamellae, so-called 'fibres', separated by concentrations of segregated species. As in all the other systems examined, the internal texture of PEEK is based on branching and splaying *individual* lamellae. What is novel with PEEK is, however, that fractional crystallization appears not to play a significant part. If there were fractional crystallization, as happens, e.g. with shorter or more branched molecules crystallizing later in linear-low density polyethylene, then such molecules would indeed have to be found between the first-forming lamellae. But this would not imply that fractional crystallization causes spherulitic development, merely that it happens to accompany it in certain systems. The evidence presented here for PEEK supports this view, and suggests that the development of a texture (generally characteristic of spherulites) made up of branching and splaying lamellae, is independent of fractionation and segregation. The reason for lowered melting points would, therefore, be found in the physical location of the material concerned, because of the sequence of crystallization. The picture is this: the first lamellae to form do so in an unrestricted environment, branching and splaying so as to occupy, but not to fill up, the available space. For subsequent crystallization the environment is changed, certainly because of less available space, but also because certain molecules may already be partly bound in the first lamellae, and the conformations and orientations allowed to their uncrystallized segments are to a degree predetermined. Moreover, molecules may thereafter be found in more than one lamella and entangled loops may be drawn tight. Under such conditions one might reasonably expect the observed slower crystallization and less stable crystallites. Such processes will give the resulting composite solid a texture in which lamellae will tend to be immersed in a non-crystalline matrix giving an overall low crystallinity, rather than the compact series of lamellae characteristic of linear polyethylene. They are most likely to be prominent, therefore, in polymers in which crystallization is inherently difficult.

Comparison with other polymers

This argument is completely general, given this type of spherulitic organization, which has been shown to be widespread. However, in polymers which only reach low levels of crystallinity, and which have broad melting endotherms, the scope for increase of crystallite size and perfection by annealing is much greater.

If we therefore examine the situation in other polymers, isotactic polystyrene is representative of a class of medium crystallinity polymers, and is well known to show two or three melting peaks of which the lowest-melting, just above T_c, is assigned to 'secondary crystallization', while the second and third peaks are assigned to the main primary population, reorganizing in a polyethylene-like manner[21–23]. This polymer can thus be said to show phenomena related both to polyethylene and to PEEK. It differs from PEEK, in that the second peak, attributed to the unreorganized melting of its primary population of broad, well-formed hexagonal lamellae[24] melts at a temperature which increases regularly by ≈ 0.5 K for every 1 K increase in T_c. Poly(ethylene terephthalate), however, has previously had its melting behaviour interpreted solely in a polyethylene-like manner[5,6]. We have re-examined this polymer[32] and, from work to be published elsewhere, believe that its phenomenology lies between that reported here for PEEK and that of isotactic polystyrene.

CONCLUSIONS

The conclusions of this paper are:

(1) That the two melting peaks normally present in crystalline PEEK represent different components of the morphology. Reorganization during heating, though present to a limited extent for the upper peak, is not the cause of there being two peaks.

(2) The broad upper melting peak represents material laid down initially, even though in the case of crystallization from the glass, this has a maximum some 150 K above T_c.

(3) The lower melting peak arises, when heating from the glass to temperature T_a, from reorganization of crystallites originally melting below T_a, together with any additional crystallization from the still rubbery phase.

(4) In the case of crystallization from the melt at T_c, the lower peak represents crystallites just stable at T_c, established slowly as the system explores all available routes to stability.

(5) It has been shown to be the case for crystallization from the melt, and is probably true in general, that first-formed lamellae have the highest melting points. Material giving the lower melting peak lies between them.

(6) This correlation of melting point variation and the separation of individual primary lamellae in the spherulite, reflects the progressively changing environment as crystallites form within spherulites. Fractional crystallization, which accentuates this effect in polyethylene, is not believed to be important in these experiments on PEEK. Instead one sees for spherulites in PEEK a characteristic lamellar structure, exhibiting a systematic variation of properties and formed independently of fractional crystallization.

(7) It is probable that similar spatial variation of properties due to sequential crystallization within spherulites should be apparent in other polymers, notably those of low crystallinity with broad melting endotherms. This appears to be so in *i*-polystyrene and polyethylene terephthalate.

Note. Since this work was largely completed, work has been published by Cebe and Hong[25] and Wunderlich *et al.*[26]: both groups of authors support the hypothesis of two distinct populations formed by two separate crystallization processes, and Wunderlich shows a set of endotherms very similar to *Figure 3b*.

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