polymer review

Thermal stability and crystallization of poly(aryl ether ether ketone)

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The molecular weight distribution of poly(aryl ether ether ketone) (PEEK) has been measured as a function of the melt holding temperature and time, in air and in an inert environment. A branching mechanism was observed to occur in the usual melt processing conditions, which was much stronger in air than in vacuum or nitrogen. This degradation mechanism is correlated to a volatile emission observed with thermogravimetric analysis. The influence of the degradation on the PEEK crystallization is discussed. A considerable decrease in crystallization rate is observed associated with the decreased molecular mobility due to the molecular weight increase, and a crystallinity decrease associated with the structural defects introduced along the chains by the branching process. The self-nucleation in PEEK has also been examined through optical microscopy. It was concluded that to get rid of the self-nucleation phenomenon, it is necessary to bring the polymer to temperatures where degradation is already present.

(Keywords: PEEK; thermal degradation; crystallization kinetics; gel permeation chromatography; thermogravimetric analysis)

INTRODUCTION

The recent development of new thermoplastic polymers with improved temperature and solvent resistances has led to a considerable interest in some highly demanding fields, such as aerospatial and aeronautic applications, because of their potential use as matrices for high performance composites. Among these materials, poly(aryl ether ether ketone) (PEEK) shows exceptional properties due to its semicrystalline character and the high molecular rigidity of its repeating unit (*Figure 1*). PEEK has a glass transition temperature (T_g) around 140°C[1], is insoluble in most common organic solvents[2], has high toughness[3,4] and low water uptake[5,6] which makes it very attractive as a high performance matrix for unidirectional continuous carbon fibre prepregs.

The heat resistance of PEEK, which is essentially due to its semicrystalline character and to its relatively high T_g, is parallel with a high melting point (around 340°C), which can be a processing limiting factor. Processing of PEEK requires temperatures around 400°C[7,8] and at such high temperatures the thermal stability of the polymer chemical bonds is questionable. Degradation of the polymer during melt processing would result in molecular modifications, which in turn would affect its crystallization behaviour and consequently the final morphology. This would ultimately change the structural properties of the final product. It is therefore of prime technological importance to evaluate the thermal stability of PEEK and to choose reasonable processing conditions.

A more fundamental interest in the determination of the thermal stability of PEEK is connected with the study of suitable melt conditions ensuring that all the crystalline remnants are destroyed without polymer degradation, is a first step to be performed before any other measurement. Various studies[9–11] have investigated the influence of PEEK melt holding conditions on its crystalline behaviour; degradation has been sometimes suggested to occur on the basis of the observed crystallization rate decrease connected with more extreme melting conditions. Thermogravimetric experiments have also been performed on PEEK[10,12–14]. However, a quantitative molecular weight analysis of the polymer after various melt holding conditions has not been performed up to now. The principal aim of this paper is to examine precisely the PEEK molecular modifications following various melt holding conditions, and to relate them to its crystalline behaviour.

EXPERIMENTAL

PEEK powder, grade 150P, was obtained in reactor powder form from ICI (Wilton Centre, UK). It was dried overnight at 150°C prior to any measurement.

Gel permeation chromatography (g.p.c.)

Approximately 1 g of PEEK powder was put into 5 mm i.d. glass tubes. Some of the tubes were sealed under low vacuum (±100 Pa) while the others were left open. The tubes were placed horizontally together with

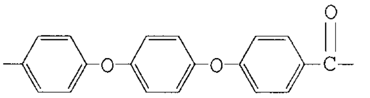

Figure 1 PEEK repeating unit

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a chromel–alumel thermocouple in an air oven at the holding temperature, T_{hold}, during the holding time, t_{hold}. The actual temperature, monitored using a Keithley 195A microvoltmeter, was found to be reproducible and stable to within ±5°C. However, the temperature fell upon introduction of the sample into the oven and the time needed to return to thermal equilibrium was observed to be ~5 min. To study the effect of the sample surface to volume ratio on the oxidative thermal degradation of PEEK, some samples were also prepared simply by spreading the reactor powder on an aluminium plate and placing it into the oven (these samples are subsequently referred to as high surface to volume samples).

It has already been shown[15] that PEEK is reproducibly and completely sulphonated by concentrated sulphuric acid in under 15 days; no molecular weight variation can be detected for dissolution times in sulphuric acid up to 3 months. Moreover, the room temperature g.p.c. of fully sulphonated PEEK in *N*-methyl-2-pyrrolidone (NMP) gives the same results as the more usual high temperature g.p.c. of unmodified PEEK in a 50/50 phenol/trichlorobenzene solution at 115°C[15]. The samples were dissolved in concentrated H_2SO_4 during at least 15 days. They were then filtered to collect insoluble residues, if any. The isolation of the residues from the filter was difficult so that they could not be accurately weighed. The soluble sulphonated fraction was precipitated in a 50/50 concentrated HCl/water solution, rinsed, dried and dissolved in distilled NMP. After addition of LiCl to suppress the ionic interactions of the sulphonated phenyls, room temperature g.p.c. of the solutions was performed on two successive Shodex columns (AD-80M/S and AT-80M/S), using an ultraviolet detector fixed at 270 nm. The calibration was performed using an iterative method, as described elsewhere[16]. The maximum uncertainty of the molecular weights was estimated to be ±10%.

Differential scanning calorimetry (d.s.c.) experiments

Non-isothermal crystallizations were performed on a Perkin-Elmer differential scanning calorimeter (usually a DSC2 and occasionally a DSC7) calibrated with indium and zinc, and operated under a constant nitrogen flux. From 7 to 12 mg of the PEEK powder was weighed in open aluminium d.s.c. pans. When performing experiments under nitrogen, the samples were put at ambient temperature in the d.s.c. furnace and were allowed to stand at this temperature for 10 min in the closed furnace to evacuate air. The samples were then heated at $320°C\ min^{-1}$ to a chosen T_{hold} and held in the molten state at this temperature for a chosen t_{hold}. A scan was then recorded from T_{hold} to ambient temperature at a rate of $-10°C\ min^{-1}$. When conducting experiments under air the sample was put in the d.s.c. furnace, which was not closed, heated at $320°C\ min^{-1}$ to T_{hold} and held in the molten state under air during t_{hold}. The d.s.c. furnace was then closed, and finally the scan was recorded under nitrogen from T_{hold} to ambient temperature at a rate of $-10°C\ min^{-1}$. The T_{hold} values varied from 385 to 440°C, while t_{hold} was kept between 5 min and 30 min. For each experiment, crystallization kinetics was evaluated by computing the crystallization temperature on cooling as reflected by the maximum in the crystallization exotherm ($T_{\text{cc,max}}$) and by the onset of this exotherm ($T_{\text{cc,ons}}$); the degree of crystallinity was estimated by the crystallization enthalpy (ΔH_{cc}). Unless otherwise stated, five different samples were prepared for each experiment and the results averaged to reduce experimental dispersion. Within the same d.s.c. cell calibration, the maximum relative uncertainty was found to be ±0.9°C for PEEK $T_{\text{cc,ons}}$, ±1.2°C for $T_{\text{cc,max}}$ and $\pm 1.2\ J\ g^{-1}$ for the ΔH_{cc}, derived from computed standard errors of 0.3°C, 0.4°C and $0.4\ J\ g^{-1}$, respectively. When comparing results obtained using different d.s.c. cell calibrations, an additional uncertainty of ±0.6°C and $\pm 4\ J\ g^{-1}$ has to be added to the previous imprecisions to obtain the absolute maximal uncertainties, also taking into account the systematic errors linked to calibration. Sometimes a single experiment was repeated on the same sample pan without any change. The relative imprecision of the measurement is thought to be then of the order of 0.2°C and $0.5\ J\ g^{-1}$.

Some isothermal crystallizations were also performed under nitrogen in the same d.s.c. apparatus. Conditions are identical to those described above, except that in place of cooling the sample from T_{hold} to ambient temperature at a constant rate of $-10°C\ min^{-1}$, the sample was quickly cooled at $320°C\ min^{-1}$ to a chosen crystallization temperature, T_c, and held at this temperature while recording the crystallization exotherm as a function of time. The recorded thermograms always presented an instability period of the order of 1 min, probably due to thermal equilibration or to an electronic transfer function. For the lowest degrees of supercooling ($T_c > 320°C$) this instability was only weakly superimposed on the crystallization exotherm, since the crystallization was very slow. It was then possible to compute the crystallization half-time ($t_{1/2}$) by numerically integrating the exotherm after having subtracted a previously run baseline. For these experiments, an Avrami analysis was sometimes also performed. It must be emphasized that at such low degrees of supercooling, the heat flux is small and the precision is reduced. In these experiments, the time was counted from the beginning of the crystallization exotherm. For higher supercooling ($T_c < 320°C$) the beginning of the exotherm was partially masked by the instability. To obtain $t_{1/2}$, the exotherm was roughly constructed in the way shown in *Figure 2*. The initial portion of the crystallization exotherm was approximated by a straight line and extended to the horizontal baseline drawn from the end of the exotherm. Time was counted from the intersection of these two lines.

Thermogravimetric experiments

Thermogravimetric experiments were conducted in a Perkin-Elmer TGA2 thermomicrobalance under nitrogen or dry air flux. To estimate the role of the sample surface to volume ratio in the degradation each experiment was repeated with three different initial weights: 5, 10 and 15 mg (±0.5 mg) in a platinum pan of constant surface. The variation of the initial sample weight without any change in the free surface of the polymer in the molten state enabled various surface to volume ratios to be obtained. After stabilization at ambient temperature over 15 min, the sample was heated at $200°C\ min^{-1}$ and held at 200°C for 15 min (to eliminate last traces of volatile, water, etc.) then heated to T_{hold} for 1 h. The weight loss for different holding times was then calculated relative to the weight measured at the beginning of the T_{hold} isotherm.

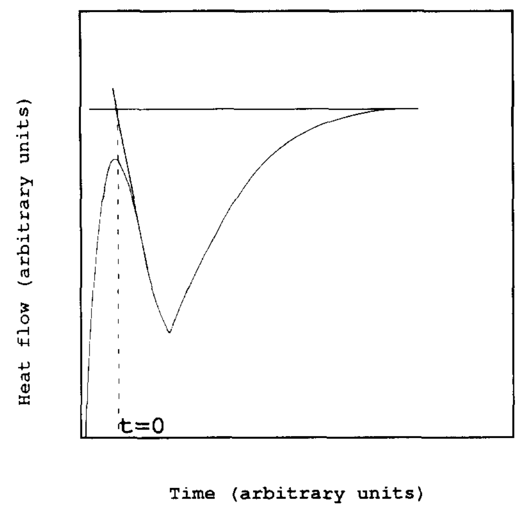

Figure 2 Typical d.s.c. thermogram recorded when crystallizing the PEEK at temperatures <320°C from the molten state. An instability perturbates the beginning of the exotherm; to estimate $t_{1/2}$, the thermogram is corrected in the way shown. The broken line represents the moment from which time is counted. For lower supercoolings, the instability is terminated before the exotherm begins to rise; no correction is therefore applied for such cases and the time is counted from the beginning of the exotherm

Using this procedure on a thermally stable inorganic substance (alumine), a gradual increase in the recorded weight loss with time was observed in nitrogen, with a slope gradually decreasing before becoming horizontal around 0.1% weight loss. This was attributed simply to a curvature of the instrument baseline. To correct for this curvature, a correctly drawn baseline has to be subtracted from the weight loss of each sample. The chosen baseline is the PEEK apparent weight loss in nitrogen at 400°C. It was found that there is no difference between the apparent PEEK weight losses measured in nitrogen at 385, 400 and 420°C. These losses cannot therefore be due to a chemical degradation or to a physical evaporation, which are thermally activated processes. They were therefore chosen as the best estimate of the thermogravimetric analysis (t.g.a.) baseline and thus subtracted from other experiments to obtain the true weight loss.

Optical microscopy

A Stanton Redcroft hot stage with a constant weak argon flux was first calibrated by sandwiching between two thin microscope slides a chromel–alumel thermocouple (each wire has a diameter of $<100\,\mu$m) embedded in a thin layer of previously molten PEEK. To compare the nucleation density for different melt conditions it was found necessary to use thin polymer films of the same approximate thickness. Such thin films of PEEK were readily obtained using the following procedure: 1 wt% PEEK was quickly dissolved in boiling phenol at 182°C, then a thin film of this solution was cast on a heated microscope slide. The phenol was almost immediately evaporated and left a thin continuous film of PEEK which was rinsed with acetone and finally dried under vacuum at 150°C. These films were then cut and put in the hot stage between two thin glass slides. The hot stage was first kept at ambient temperature for 20 min, which was estimated to be sufficient to purge the system with argon, heated at 100°C min^{-1}, held at T_{hold} for t_{hold} under argon, then cooled to 312°C at -100°C min^{-1}. The films were quenched in cold water after 5 min crystallization at 312°C. The morphology was then observed using a polarizing optical microscope.

RESULTS

A representative molecular weight distribution of the as received PEEK powder used in this study is given in *Figure 3*. Average g.p.c. results (six different samples) gave $M_n = 10\,300$ g mol^{-1}, $M_w = 26\,800$ g mol^{-1} and $M_z = 52\,200$ g mol^{-1}. It is important to note the presence of a low molecular weight peak in the distribution. The average peak molecular weight of this oligomer peak was found to be around 1750 g mol^{-1}, which is roughly the 6-mer molecular weight. A quantitative fluor analysis was performed by nuclear magnetic resonance on the polymer in concentrated sulphuric acid in order to check that the chains were fluor-terminated on both sides, following a method given elsewhere[17]. Two measurements performed on two different batches of the same polymer grade (PK150P) gave a chain-end fluor weight concentration of 2130 ± 10 ppm. This is much lower than the value of 3690 ppm which is expected from the M_n value determined by g.p.c. if every chain end was fluor-terminated. Other possible chain ends are phenolic or phenolate groups from the synthesis[18] or even monosubstituted phenyl if phenyl-terminated reagents are added at the end of the synthesis. The knowledge of the chain end nature of a given grade of PEEK can be important with regard to the crystallization phenomena of this sample. It has been shown previously[19] that even quite small amounts of specific chain ends can considerably increase the crystallization kinetics of PEEK. Further work has still to be done to precisely identify all the chain end groups present in PK150P. Cation elemental analysis of the polymer was also performed and the results are given in *Table 1*. Noticeable

Table 1 Elemental analysis of PK150P (weight concentration of cations)

Cation	Al	Ca	Fe	K	Na	P
ppm	9	45	10	–	110	34

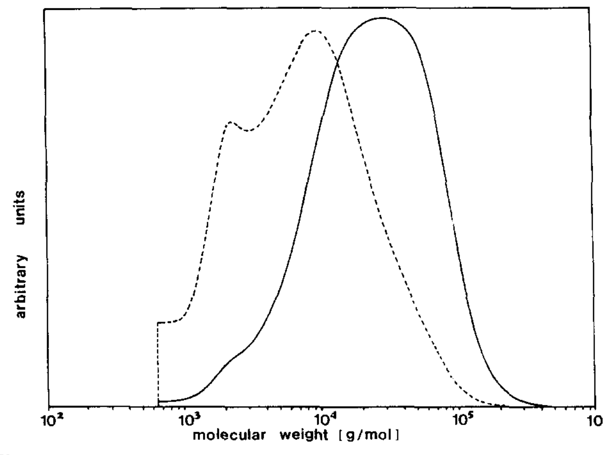

Figure 3 Number (——) and weight (— - —) molecular weight distributions of the fully sulphonated PEEK powder, obtained at room temperature by g.p.c. in NMP. The molecular weights must be divided by 1.299 to obtain the PEEK molecular weights before sulphonation. Note the presence of an oligomer peak in the distributions, centred around the 6-mer mass. The averaged molecular weights are: $M_n = 10\,300$ g mol^{-1}; $M_w = 26\,800$ g mol^{-1}; $M_z = 52\,200$ g mol^{-1}

amounts of sodium were observed, due probably partly to the presence of NaH_2PO_4/Na_2HPO_4 which is a known buffer used to protect the polymer against the acid–base attacks, and partly to synthesis residues (Na_2CO_3 or NaF) or perhaps a few phenolate chain ends.

Table 2 gives the PEEK molecular weights as a function of t_{hold} in the melt under vacuum or in air for various T_{hold} values. There can hardly be seen any modification in the PEEK number molecular weight for t_{hold} values as long as 30 min in air or in vacuum, at least in the g.p.c. precision limits. The results for M_w and M_z are also presented in *Figure 4*. It appears that M_w must be considered as constant for the vacuum melt conditions of this study, whereas M_z shows a small but significant trend to rise with t_{hold} at 440°C under vacuum. When the polymer is molten in air, M_w and M_z strongly increase with t_{hold} in the melt, showing a dramatic rise for the highest T_{hold} (440°C). The degradation mechanism is already noticeable at temperatures as low as 385°C in air. No insoluble residues were observed after the sulphonation of the vacuum molten samples but insoluble residues were found for some of the air molten samples. A rough evaluation of the amount of these insoluble residues is also given in *Table 2*. When these insoluble fractions appear, M_w and M_z reach almost constant values, because insoluble fractions are not taken into account with g.p.c. The PEEK thermal degradation in air or in vacuum is thus characterized by an increase in M_w and M_z without any variation in M_n and leads ultimately to crosslinking. A progressive branching mechanism is clearly operative at usual processing temperatures in air and at 440°C in vacuum.

When the sample surface to volume ratio is increased (powder spread on aluminium), a parallel increase in the degradation rate in air is observed (*Figure 5*). At such high surface to volume ratios a significant amount of insoluble residue already appears after 30 min melting at 400°C or after 15 min at 420°C. The influence of the surface to volume ratio on the degradation rate in air is evidence that the diffusion of oxygen into molten PEEK from its free surface is one of the degradation controlling parameters. For a given air t_{hold}, the higher the surface to volume ratio, the bigger the oxygen diffusion zone compared to the total sample volume, the bigger the thermo-oxidative degradation zone and the higher the measured molecular weights, which are values averaged on the total sample volume. The amount of degraded polymer is thus partly controlled by the oxygen diffusion.

Turning now to the t.g.a. results under nitrogen, no significant difference in the relative weight loss of samples was observed for three various initial surface to volume ratios. It was therefore decided to take for each (T_{hold}, t_{hold}) condition the mean of the three measurements made with different surface to volume ratios.

The same experiments performed under air revealed a strong dependence of the volatile evolution on the initial sample surface to volume ratio. For instance, *Figure 6a* gives the PEEK relative weight loss measured at 440°C under air as a function of time for three samples of constant free surface (i.e. the surface exposed to air) but of different initial volumes, while *Figure 6b* is the absolute weight loss in the same conditions (i.e. the relative weight loss multiplied by the initial sample weight). Although the relative losses change dramatically when the initial surface to volume ratios are varied, the absolute losses expressed in milligrams are more or less equivalent. Same observations can be made for the other T_{hold} values (385, 400 and 420°C). Thus the amount of volatile emission in air is not proportional to the sample volume but depends more on the sample free surface. The major part of the volatiles emerges thus essentially from a polymer layer of roughly the same thickness whatever the initial sample thickness.

As stated earlier, no significant weight loss could be measured in nitrogen at 385, 400 and 420°C. At 440°C, the weak evolution of a volatile can be clearly observed (*Figure 7*), having a linear dependence with time and a weight loss constant around $1.7 \times 10^{-3}\%\ \mathrm{min}^{-1}$ ($2.8 \times 10^{-7}\ \mathrm{s}^{-1}$). This behaviour has to be linked to the evaporation of a degradation product or a high boiling point volatile present in PEEK. Such a volatile could be a residue from the synthesis, i.e. diphenylsulphone (DPS) which is the synthesis solvent or perhaps even a very low molecular weight oligomer.

To check the presence of DPS, a finely ground PEEK powder was washed with acetone in a Soxhlet during 93 h. Using infra-red (i.r.) spectroscopy (with a multiple internal reflection cell) some very weak traces of DPS

Table 2 PEEK molecular weights obtained after melting in vacuum or in air during t_{hold} at T_{hold}. Also given, the rough insoluble weight concentration after melting in air and subsequent dissolution–sulphonation in H_2SO_4

T_{hold} (°C)	t_{hold} (min)	M_n ($\mathrm{g\,mol^{-1}}$, vac.)	M_w ($\mathrm{g\,mol^{-1}}$, vac.)	M_z ($\mathrm{g\,mol^{-1}}$, vac.)	M_n ($\mathrm{g\,mol^{-1}}$, air)	M_w ($\mathrm{g\,mol^{-1}}$, air)	M_z ($\mathrm{g\,mol^{-1}}$, air)	Insolubles (air, %)
–	–	10 300	26 800	52 200	10 300	26 800	52 200	–
385	5	11 800	26 200	45 800	10 400	27 750	55 400	–
385	15	9 900	26 500	51 900	9 800	27 850	58 350	–
385	30	10 400	27 000	53 000	10 400	28 200	60 950	–
400	5	10 100	26 000	49 600	11 050	27 400	53 000	–
400	15	10 100	26 900	53 000	10 850	27 200	52 700	–
400	30	11 200	28 300	54 200	9 750	28 750	66 600	–
420	5	11 500	27 400	50 000	10 450	25 800	48 900	–
420	15	9 400	27 200	55 900	10 150	27 000	55 550	–
420	30	10 300	27 600	54 600	10 800	30 800	84 100	1.7
440	5	10 800	26 900	50 500	11 150	26 600	49 700	–
440	15	10 200	27 000	54 400	10 250	30 650	82 100	4.7
440	30	11 200	28 300	57 600	11 300	30 550	82 500	2.2

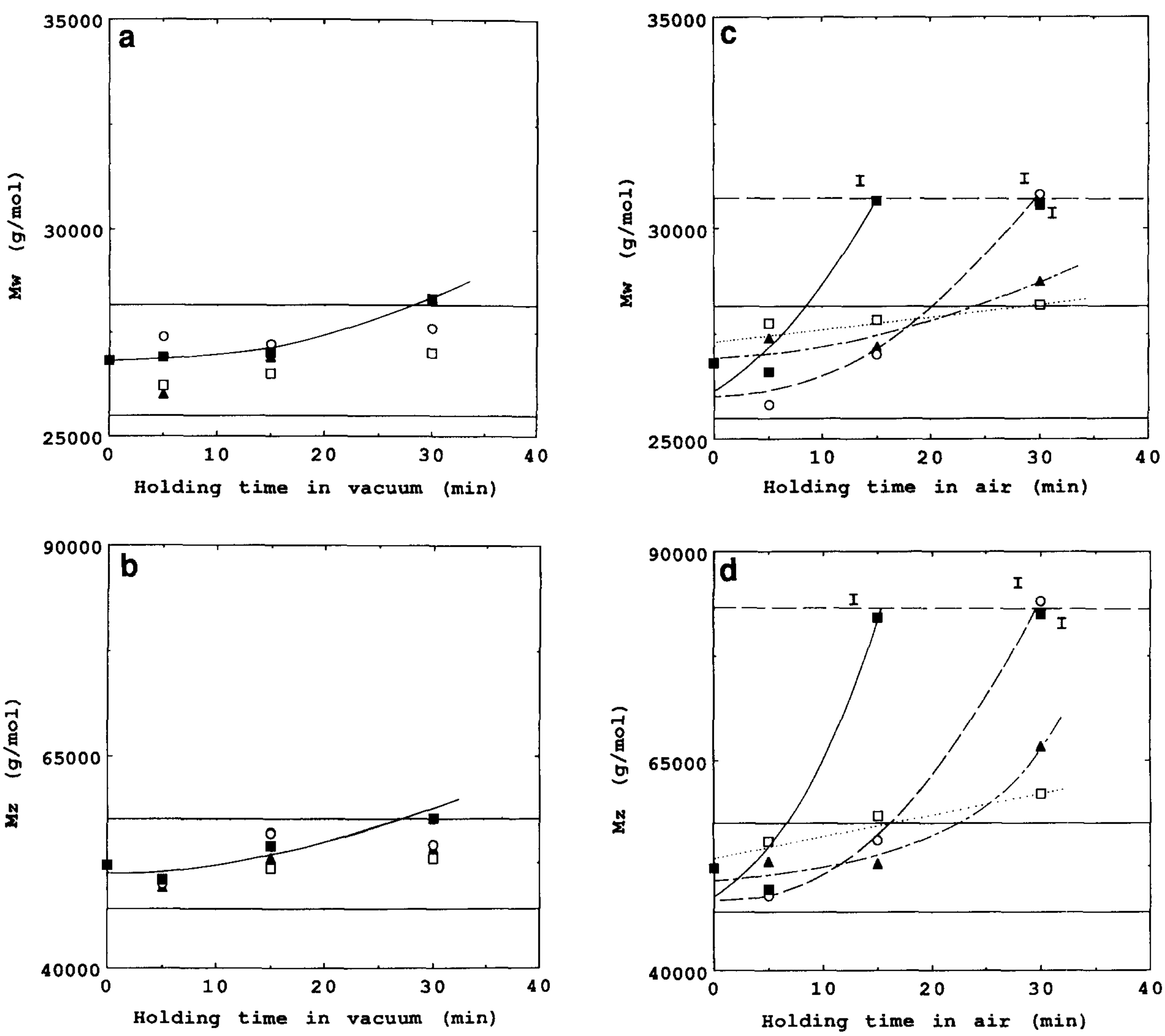

Figure 4 M_w and M_z as a function of the holding time in the molten state in vacuum ((a) and (b)) or in air ((c) and (d)). When insolubles are present in the solution, the symbol I is drawn near the relevant point. The solid lines represent the estimated maximum uncertainty interval around the mean values for the as-received polymer. The melt holding temperatures are: □ · · · · · □, 385°C; ▲——▲, 400°C; ○--○, 420°C; ■——■, 440°C

were found in the filtered extracted solution but were too weak to explain the observed continuously rising weight loss. Interesting to note is that PEEK i.r. bands were also found in the i.r. spectrum of the filtered extracted solution and that upon concentration of this solution a precipitate appeared having precisely the PEEK i.r. spectra. A g.p.c. analysis was performed on this precipitate (at 115°C in a 50/50 w/w phenol/trichlorobenzene solvent, using 1 UltraStyragel 500 Å and 2 Shodex mixed-bed columns); the chromatogram showed two peaks with retention times between the retention times of the fluor-terminated monomer ($F\Phi CO(\Phi O\Phi O\Phi CO)_1\Phi F$) and 3-mer ($F\Phi CO(\Phi O\Phi O\Phi CO)_3\Phi F$)*. Work is currently in progress to gain further insight into these PEEK oligomers weakly soluble in acetone. This experiment confirms the existence of very low molecular weight oligomers in PK150P.

Table 3 Onset of weight loss of PEEK and some low molecular weight oligomers of PEEK (t.g.a.: 10°C min^{-1} from 50 to 900°C, nitrogen atmosphere[20]). The weight loss is due to a simple evaporation when the t.g.a. pan is totally empty after the temperature scan, or degradation leading partly to volatilization of by-products when carbonaceous residues are found in the t.g.a. pan after the scan

Chemical formula[a]	Molecular weight (g mol^{-1})	Onset of evaporation or degradation (°C, ±10°C)	Carbonaceous residues at 900°C (%)
$F\Phi CO\Phi F$	218	195	0
$F\Phi CO(\Phi O\Phi O\Phi CO)_1\Phi F$	507	403	3
$F\Phi CO(\Phi O\Phi O\Phi CO)_2\Phi F$	795	498	14
$F\Phi CO(\Phi O\Phi O\Phi CO)_n\Phi F$ (PK150P)	10300	584	41

[a] Φ represents a *p*-disubstituted phenyl group

Table 3 gives the onset temperature at which very low molecular weight fluor-terminated PEEK oligomers begin to lose volatiles in nitrogen as measured by t.g.a.[20] at 10°C min^{-1}. From these results it seems probable that the fluor-terminated monomer ($F\Phi CO(\Phi O\Phi O\Phi CO)_1\Phi F$) evaporates at temperatures around 400°C, without appreciable degradation, since the amount of carbonaceous residues left after heating is almost zero. The evaporation temperature of the higher

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* Φ is taken here as the symbol of a *p*-disubstituted phenyl

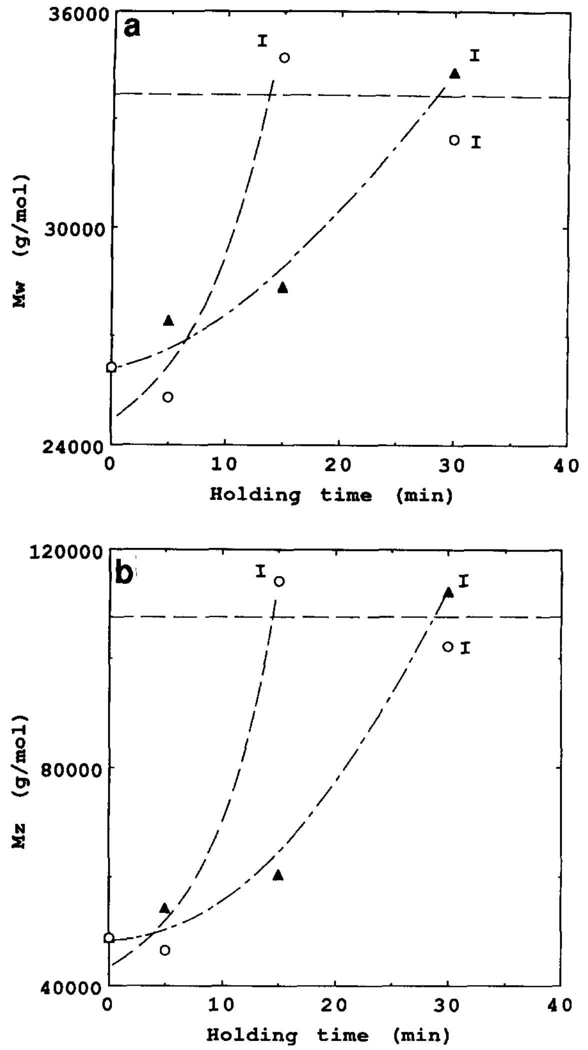

Figure 5 M_w and M_z of high surface to volume ratio PEEK samples as a function of the melt holding time in air. The melt holding temperatures are: ▲——▲, 400°C; ○--○, 420°C

molecular weight oligomers must therefore be much higher than 400°C. The weight loss onset temperature for the next oligomer ($F\Phi CO(\Phi O\Phi O\Phi CO)_2\Phi F$) is of the order of 500°C. This is obviously too low to be the evaporation temperature of this dimer, in view of the previous result for the monomer. The dimer weight loss must therefore be due to a thermal degradation leading to evaporation of by-products; this is confirmed by the fact that an important carbonaceous residue is left after the heating scan. One can thus confirm that the monomer is the only PEEK oligomer whose evaporation without previous degradation can be possible at 440°C. Because it is doubtful that the monomer content of PK150P reaches such high levels as 0.1 wt% (see the weight molecular distribution of the polymer, *Figure 3*), the recorded volatile evolution of PK150P at 440°C in nitrogen can actually be attributed to the departure of a degradation product and not to genuine monomer evaporation. Recall that the degradation has also been observed by the increase in M_z at 440°C in nitrogen. Neither t.g.a. nor g.p.c. detect however a PEEK degradation in nitrogen for T_{hold} values of $\leqslant$420°C and t_{hold} values <1 h.

Under air, volatile evolution is stronger than under nitrogen and is observed at each of the holding conditions used. *Figure 8* shows the absolute air kinetic degradation

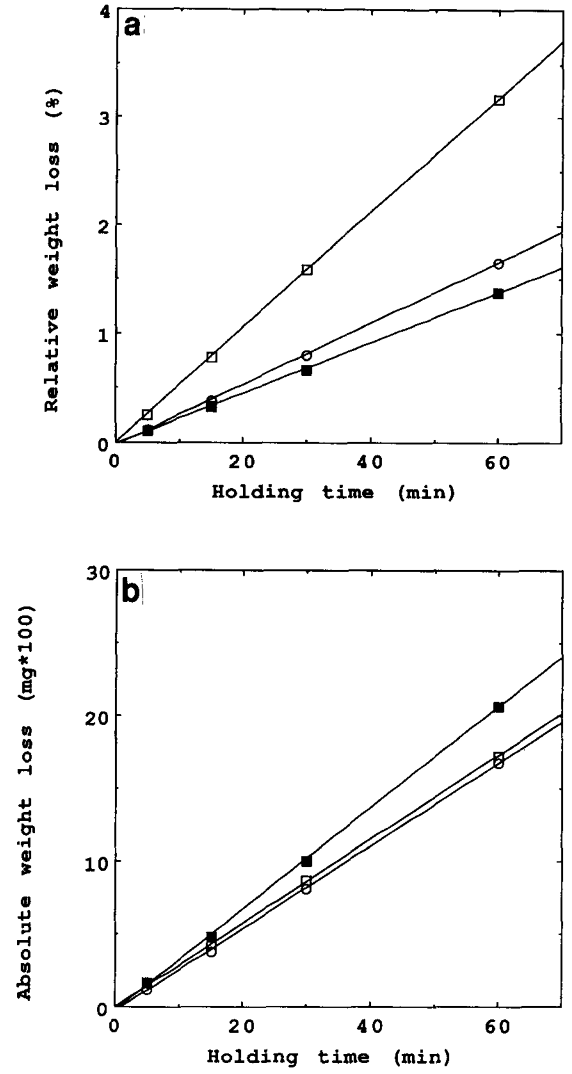

Figure 6 PEEK weight loss in air at 440°C as a function of the melt holding time. Various initial polymer weights have been put in a t.g.a. pan of constant surface; 5 mg (□), 10 mg (○) and 15 mg (■). This led to different surface to volume ratios, the highest ratio being linked to the lowest initial sample weight. In (a) the relative weight loss (%) is seen to be a strong function of the initial sample weight. In (b) the absolute weight loss (mg) can be considered to be only weakly dependent on the initial sample weight

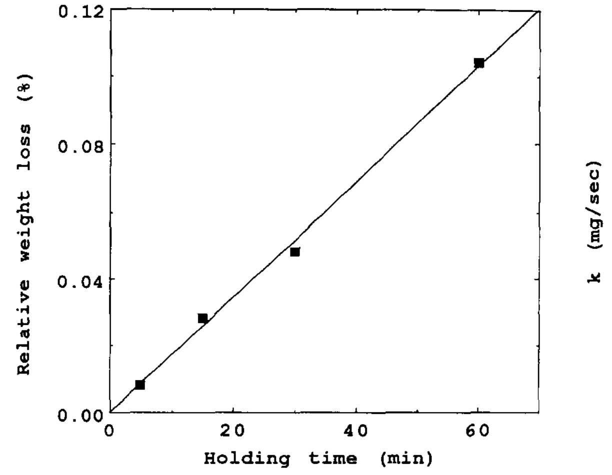

Figure 7 PEEK relative weight loss in nitrogen at 440°C after baseline correction

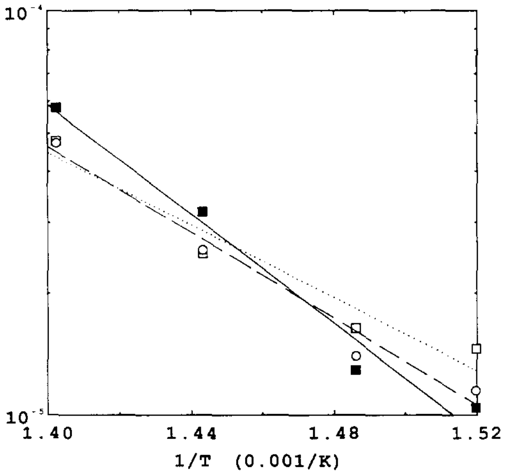

Figure 8 Arrhenius plot of the kinetic degradation constants for PEEK in air ($k = \mathrm{d}\Delta P/\mathrm{d}t$ where ΔP is the absolute weight loss and t the melt holding time). The results are given for the three initial sample weights used in this study: □·····□, 5 mg; ○—○, 10 mg; ■—■, 15 mg

Table 4 Calculated activation energies for the PEEK weight loss in air, between 385°C and 440°C, as a function of the initial sample weight

Initial weight (mg)	E_a (kJ mol^{-1})
5	85
10	102
15	128
Mean	105 ± 25

constants (k, mg s^{-1}) as a function of the melt temperature, calculated from the weight loss curves which were found to be linear with time (*Figure* 6). There is some scatter in the results; the calculated activation energies (E_a) change with the initial sample weight, the mean value being 105 ± 25 kJ mol^{-1} (*Table 4*). Earlier it was shown that the degradation kinetics are controlled by oxygen diffusion. The amount of volatile evolution is a complex function of the oxygen diffusion rate into molten PEEK, of the thermodegradation kinetics and of the rate of the degradation products diffusion to the free surface. Moreover, this last diffusion is eventually complicated by supplementary reactions that the degradation products (e.g. radicals) could undertake with the polymer during their diffusion path to the free surface. The calculated E_a values are thus functions of many closely successive processes and are therefore only apparent E_a values. It was also shown that most of the volatiles are essentially emitted from a polymer layer of roughly the same thickness whatever the initial sample thickness. The weak dependence of E_a on the sample volume results from the smaller amount of volatiles emitted from deeper inside the polymer sample.

The process of PEEK degradation that emerges is the following. The degradation always results in M_w and M_z increases with volatiles emission. The degradation rate is significantly lower in the absence of oxygen and the oxygen diffusion is one of the rate controlling parameters. This implies that the degradation in air is more intense at the sample surface than in the bulk of the sample. The volatiles emitted after a given degradation time emerge roughly from the same depth whatever the sample thickness. This can be considered to be due to the lower bulk degradation compared to the surface degradation, a direct consequence of the dependence of the degradation on the oxygen diffusion. The following will be mostly devoted to the consequence of this degradation on the PEEK crystallization.

Crystallization studies

Non-isothermal crystallization exotherms were recorded by d.s.c. after melting the polymer at 385, 400, 420 or 440°C during 5, 15 or 30 min. This set of experiments was performed using a unique d.s.c. calibration. The general observed trend is a decrease of the crystallization rate with increase of the melt t_{hold} or T_{hold} values. (*Figure 9* is a three-dimensional interpolation plot comparing the crystallization temperature as a function of the holding conditions in air and in nitrogen.) The decrease of the crystallization rate with the holding conditions parallels the branching process and the volatile evolution discussed above. There is a large difference in the decreasing crystallization rates of the polymer molten in an inert or an oxidative atmosphere.

Table 5 details the crystallization temperatures and crystallization enthalpy as a function of T_{hold} and t_{hold} in the melt under air. These results are averaged values, not taking into account the influence of the surface to volume ratios because of the weak variation of this ratio for the sample weights used in the d.s.c. pans. In air, the crystallization rate decrease is already strongly effective even for short t_{hold} values above 400°C or after 15 min melting at 385°C. The end-of-run crystallinity (ΔH_{cc}) can also be seen to decrease dramatically with t_{hold} and T_{hold}. The branching mechanism evidenced by

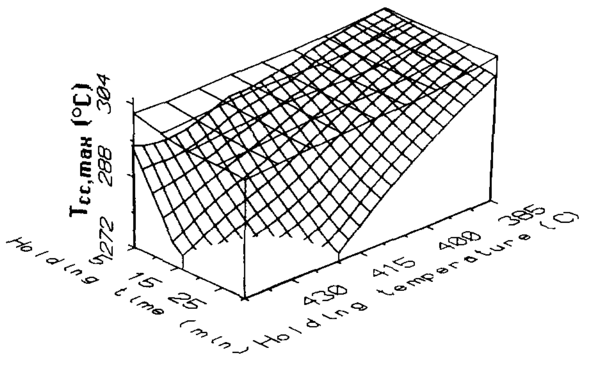

Figure 9 Interpolation plot showing the variation of the PEEK crystallization temperature ($T_{cc,max}$) with the melt holding conditions. The upper curve has been obtained in nitrogen, the lower in air

Table 5 PEEK crystallization temperature and crystallization enthalpy measured at a cooling rate of 10°C min^{-1}, as a function of t_{hold} and T_{hold} in the melt under air

T_{hold} (°C)	t_{hold} (min)	$T_{cc,ons}$ (°C)	$T_{cc,max}$ (°C)	ΔH_{cc} (J g^{-1})
385	5	312.7	305.1	46
385	15	311.7	303.6	46
385	30	309.2	300.3	44
400	5	312.2	302.2	46
400	15	308.9	298.1	46
400	30	303.5	290.4	44
420	5	310.0	298.0	46
420	15	306.1	286.8	43
420	30	299.5	273.0	35
440	5	310.5	294.9	46
440	15	304.4	275.8	35

g.p.c. to occur in air reduces thus very rapidly the overall crystal growth rate by increasing the molecular viscosity. It also creates structural defects along the macromolecular chain, reducing the ability of the macromolecule to take part in the crystalline ordered structure and causing a decrease in the attainable crystallinity (ΔH_{cc}). However, the defect concentration along the chains becomes high enough to decrease ΔH_{cc} only at a latter stage in the degradation process: an important decrease in ΔH_{cc} is indeed observed only after very severe holding conditions ($T_{hold} \geqslant 420°C$, $t_{hold} \geqslant 15$ min), although the crystallization temperatures are already strongly depressed for less severe holding conditions.

Even though the thickness of the samples in the d.s.c. pans is rather low, air degradation appears to be strongly non-uniform along the normal to the air exposed surface. This can be observed by plotting the difference $T_{cc,ons} - T_{cc,max}$ ($= \Delta T_{cc}$) as a function of t_{hold} and T_{hold} (*Figure 10*). This parameter which could be defined as a crystallization peak width, increases strongly with t_{hold} or T_{hold}. For a short melt holding time of 5 min, ΔT_{cc} is doubled when T_{hold} is scanned from 385 to 440°C. However, $T_{cc,ons}$, which is related to the beginning of the crystallization, varies only slightly (from 312.7 to 310°C). This last observation means that after 5 min melting there still exists only weakly degraded polymer which crystallizes nearly as fast as the undegraded polymer, whereas the broadening of the crystallization peak has to be linked to the existence of large amounts of degraded polymer crystallizing more slowly. This is probably due to the greater degradation at the surface sample than in the bulk, as already revealed by t.g.a. and g.p.c. For longer melting times however, the crystallization onset falls in a more pronounced way because more and more oxygen has penetrated deep into the polymer. However, ΔT_{cc} is still increasing, because the degradation mechanism is still more rapid at the surface than in the bulk.

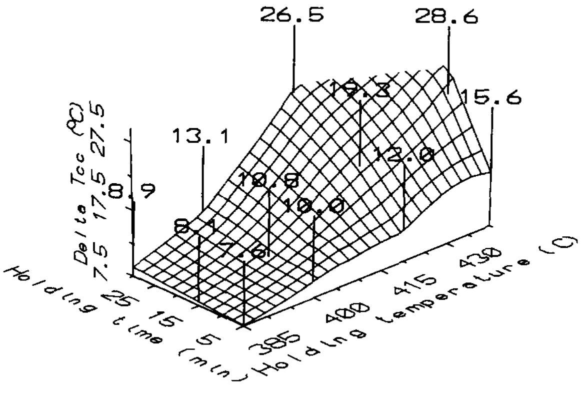

Figure 10 Interpolation plot reporting the PEEK crystallization peak width as a function of the melt holding conditions in air

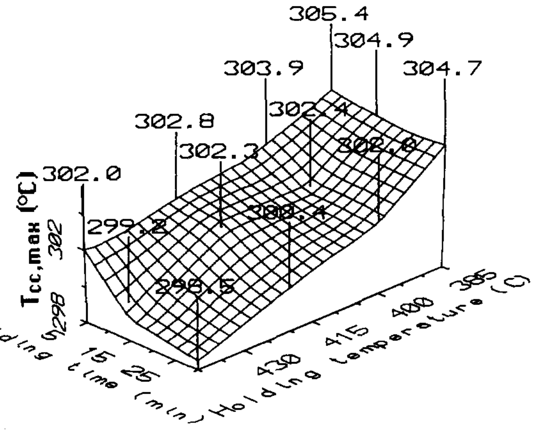

Figure 11 Interpolation plot reporting the PEEK crystallization temperature ($T_{cc,max}$) as a function of the melt holding conditions in nitrogen

Table 6 PEEK crystallization temperature and crystallization enthalpy measured at a cooling rate of 10°C min^{-1} as a function of t_{hold} and T_{hold} in the melt under nitrogen

T_{hold} (°C)	t_{hold} (min)	$T_{cc,ons}$ (°C)	$T_{cc,max}$ (°C)	ΔH_{cc} (J g^{-1})
385	5	314.2	305.4	50
385	15	313.3	304.9	51
385	30	312.7	304.7	51
400	5	313.0	303.9	49
400	15	312.9	302.4	49
400	30	312.5	302.0	49
420	5	313.5	302.8	49
420	15	312.9	302.3	49
420	30	311.3	300.4	50
440	5	312.0	302.0	49
440	15	310.5	299.2	49
440	30	309.6	298.5	47

PEEK crystallization has been shown to be less sensitive to the melting conditions in nitrogen than in air. Crystallization temperatures and crystallization enthalpy are given in *Table 6* and *Figure 11*. Although weak, a significant influence of the melt conditions can be observed. For T_{hold} values between 400°C and 420°C, the crystallization temperatures are constant within the d.s.c. uncertainty limits ($T_{cc,max} = 302$–$304°C$; $T_{cc,ons} = 312$–$313.5°C$), except for long t_{hold} at 420°C where the crystallization temperatures are lower. When the polymer is held in the molten state at 385°C the recorded crystallization temperatures are significantly higher. This is especially true for $T_{cc,max}$. Finally, for a high T_{hold} (440°C) a rapid decrease in the crystallization temperatures is observed. The end-of-run crystallinity (ΔH_{cc}) is roughly constant for each T_{hold}, except for long t_{hold} at 440°C where it begins to decrease.

For mild holding conditions ($T_{hold} = 385°C$, each t_{hold}) the crystallization kinetics are fast. To gain more insight into the physical phenomena causing this high crystallization rate, some optical microscopy experiments were performed. *Figure 12* shows the spherulitic morphology obtained on crystallizing PEEK films for 5 min at 312°C, after 5 min melting at 385°C (*Figure 12a*), 5 min at 400°C (*Figure 12b*) or 15 min at 410°C (*Figure 12c*) under argon. It is clearly shown that the number of spherulites is significantly higher upon melting at 385°C than upon melting at 400 or 410°C. However no clear difference can be observed in the morphologies of the samples molten for 15 min at 410°C or 5 min at 400°C before crystallization. Because the maximum spherulite sizes are comparable after melting at 385 or 400°C, it can be inferred that no important degradation has occurred during these meltings, and that the difference in the crystallization rate is principally due to a decrease in the nucleation density and not to a decrease of the linear growth rate of the spherulites due to degradation. By melting the polymer above 385°C, some

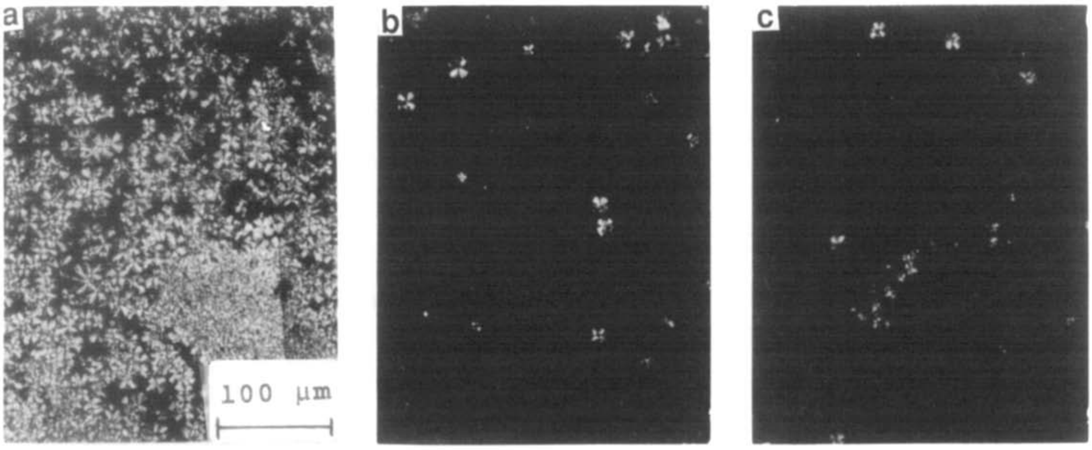

Figure 12 Optical micrographs (crossed nichols) showing the spherulitic arrangement obtained when crystallizing the PEEK for 5 min at 312°C under argon. Melt holding conditions: (a) 385°C for 5 min; (b) 400°C for 5 min; (c) 410°C for 15 min

crystallization seeds are thus destroyed. It is known[21] that minute unmolten crystalline seeds can persist in the homogeneous melt up to the thermodynamic melting point (T_m^0). When the polymer crystallizes from a temperature where all these seeds have not been destroyed, their presence decreases the crystallization free energy barrier and thus increases the crystallization rate. This phenomenon has been called self-nucleation. It can thus be stated that self-nucleation in PEEK is suppressed by heating the polymer for 5 min between 385°C and 400°C. This is the explanation for the higher crystallization rate for the 385°C holding conditions.

For severe nitrogen holding conditions ($T_{hold} = 440$°C, each t_{hold}) the crystallization kinetics are slower than for lower T_{hold} values. The crystallization rate decreases with t_{hold} in the melt, and even the crystallization enthalpy diminishes with t_{hold}, in a similar fashion as for the air holding conditions. For nitrogen treatment as well as for air treatment, the same causes have to be invoked to explain the crystallization decrease at 440°C; progressive branching leading to crosslinking. This can indeed be also inferred from the above nitrogen g.p.c. results. Recall also that a volatile evolution was observed when the polymer was held under nitrogen at 440°C. It is worth noting here that this degradation is quite weak so that it is only weakly detected using g.p.c. or t.g.a.; however, it is more easily detected using d.s.c. because of the strong dependence of the crystallization kinetics on molecular mobility.

For T_{hold} values <440°C, it is difficult to elucidate if thermal degradation is already effective because of the reduced number of measurements and because of the measurement uncertainty. No degradation could be observed for such holding conditions using g.p.c. or t.g.a., but because of the high sensitivity of the crystallization rate to the molecular viscosity it can be expected to obtain more insight into the holding conditions from non-isothermal crystallization thermograms. More detailed experiments were then performed in nitrogen to study the effect of T_{hold} on the PEEK crystallization keeping t_{hold} constant and to study the effect of t_{hold} on the crystallization keeping T_{hold} constant.

So, T_{hold} was scanned from 400 to 420°C every 5°C, while t_{hold} was kept at 5 or 15 min. The results, each being the average of five measurements, were obtained using a new unique d.s.c. calibration (*Figure 13*). Within the absolute d.s.c. uncertainty, the new results obtained after 5 min melting at 400 or 420°C are found to be equivalent to the previous measurements.

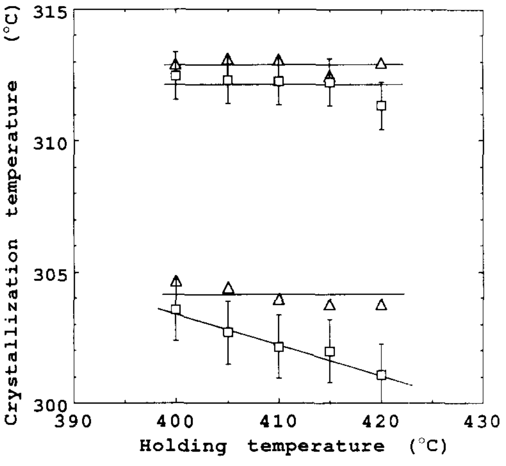

Figure 13 PEEK crystallization temperatures (onset and minimum) as a function of the melt holding temperature in nitrogen. Melt holding times: △, 5 min; □, 15 min. The error bars indicate the calculated maximum uncertainty for the T_{cc}

It can be seen in *Figure 13* that $T_{cc,ons}$ has to be considered as independent of T_{hold} within the d.s.c. uncertainty for every T_{hold} between 400°C and 420°C. This is also true for $T_{cc,max}$ when t_{hold} is 5 min. However $T_{cc,max}$ slightly but significantly decreases with T_{hold} in the molten state, when t_{hold} is 15 min.

More precise conclusions can be obtained when the dependence of the crystallization kinetics is observed as a function of t_{hold}, with T_{hold} being kept constant. It is then possible to remove the dispersion linked to the change of sample by working on a unique sample, repeatedly molten during various t_{hold} values and scanned in the d.s.c. from a fixed T_{hold} to 200°C at -10°C min^{-1}. Scans were performed in stainless steel pans because aluminium pans were found to be too ductile for repeated melting–crystallization cycles. Four T_{hold} values were chosen (385, 400, 410 and 440°C), with a new sample being taken for each of the four experiments. The results are given in *Figure 14*.

Important points to note about *Figure 14* are:

1. The T_{cc} and ΔH_{cc} are given as functions of the total t_{hold}, which is for a given scan the sum of the t_{hold} values of the previous scans, up to this last scan. However, the polymer degradation and/or the destruction of the

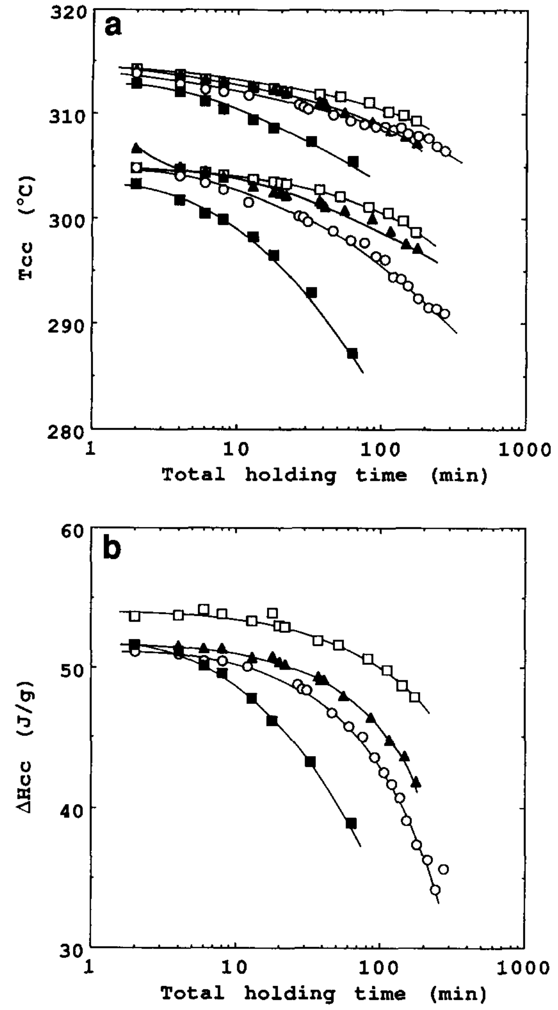

Figure 14 PEEK crystallization temperatures (a) and crystallization enthalpy (b) as a function of the melt holding time in nitrogen for repeated melting–crystallization cycles. Melt holding temperatures: □, 385°C; ▲, 400°C; ○, 410°C; ■, 440°C

crystalline seeds can be also effective during the scan time from T_{hold} to a given unknown temperature. No attempt has been done to take this supplementary time into account.

2. Imprecisions are thought to be very low inside a given curve (constant T_{hold}) of the order of 0.2°C and 0.5 J g^{-1} maximum. However, absolute imprecisions are quite high because results were obtained on one sample only without any averaging procedure. It is therefore meaningless to compare the absolute values of the curves; only comparisons of their general trends are valid.
3. The time axis is logarithmic.

The following observations can be made from inspection of *Figure 14*. When T_{hold} is 385°C, the crystallization temperatures decrease from the beginning of t_{hold}, although no ΔH_{cc} variation can be observed before the melt t_{hold} is above 20 min. When T_{hold} is 400°C, ΔH_{cc} is constant up to 10 min t_{hold}, whereas the T_{cc} decrease from the beginning; the same behaviour is observed after a 410°C melting, except that a very weak decrease in ΔH_{cc} is noticeable from the beginning of the t_{hold}. Finally, when T_{hold} is 440°C, both ΔH_{cc} and T_{cc} decrease from the beginning of the melt t_{hold}.

For each T_{hold}, a decrease in the crystallization kinetics can thus be observed from the beginning of the melt t_{hold} in nitrogen. It was shown above that a branching mechanism was operative when holding the polymer in the molten state under air. This degradation reduces the molecular mobility and therefore the crystallization temperatures and introduces structural defects on the macromolecular chains, thereby reducing the crystallization enthalpy after some time. When holding the polymer in nitrogen at 440°C, a similar branching mechanism was shown to exist on the basis of g.p.c. and d.s.c. results. This can again be observed in *Figure 14*, where both ΔH_{cc} and T_{cc} are decreasing from the beginning of t_{hold} at 440°C. Because thermodegradation is a thermally activated chemical mechanism, it must still be effective at temperatures <440°C, though at a slower rate. This is precisely what can be observed in *Figure 14* for T_{hold} values between 385°C and 410°C. There is no qualitative difference between these curves and the curves measured at 440°C; only quantitative differences exist, such as the intensity of the ΔH_{cc} or T_{cc} decreases or the minimum t_{hold} from which a ΔH_{cc} decrease can be measured. From these observations, it is possible to infer that polymer degradation is also effective in nitrogen at temperatures as low as 385°C, although quite slowly. For these low T_{hold} values no M_z increase has been measured by g.p.c. because the degradation is still weak for t_{hold} values <30 min (which was the maximum t_{hold} studied using g.p.c.), and because of the relatively poor precision of a g.p.c. technique.

However, it was shown that seed destruction is only performed by heating the polymer above 385°C. Conversely, it is expected that the number of surviving crystalline seeds can be decreased by increasing t_{hold} at 385°C. The crystallization rate decrease observed as a function of t_{hold} at 385°C, could thus also be due to a progressive crystalline seeds destruction phenomenon and not only to a molecular viscosity increase. It would be difficult to conceive that such a phenomenon could be invoked to explain the observed ΔH_{cc} decrease. However there is an induction time before which no ΔH_{cc} decrease can be observed. This does not mean that no degradation occurs during this period, since a similar induction time was noted to exist for the PEEK degradation in air. Its origin was then thought to be the insufficient amount of defects along the polymer chain to cause a crystallinity decrease, although an important T_{cc} decrease was still observed. It is also possible that during this induction time at 385°C a decrease of the nucleating seeds number is partly responsible for the crystallization rate decrease.

For T_{hold} values of >385°C self-nucleation is suppressed, and the crystallization rate decrease could be considered to be due only to polymer degradation. One could however still invoke the destruction of some very peculiar nucleating germs to explain part of the T_{cc} decrease without a ΔH_{cc} decrease. For example it is known[22] that crystalline nuclei can survive at temperatures higher than the thermodynamic melting point provided they are retained on an heterogeneous contaminant. This can be due to a negative contribution to the crystal free energy brought by the adsorption of the crystalline phase onto the heterogeneity[23] or to a smaller melting entropy associated with the restriction of the available number of conformations for the molten polymer. Heterogeneities in the PEEK powder could be ionic catalysts residues, ionic synthesis by-products or other contaminants. Such crystals stabilized on heterogeneities could appear after the synthesis, when the polymer is slowly cooled from the synthesis temperature (around 300°C) in DPS; the higher mobility of the dissolved polymer could explain the formation of such crystals. When crystallizing the polymer from the melt these stabilized germs could act as crystallization seeds, although with less efficiency than truly bulk crystalline remnants because their accessibility and conformation is questionable. Superheating the polymer could progressively melt some of these seeds, depending on their stabilization; the time needed to fully destroy such germs could be quite long. Once molten, it would be quite impossible for them to reappear from the highly viscous melt. Above 400°C the irreversible decrease of T_{cc} with t_{hold} could thus be partly associated with such a phenomenon but is also certainly associated with the beginning of the branching process.

Oligomer nucleation is another hypothesis able to partly explain the decrease of the crystallization kinetics for the short melt t_{hold}. The g.p.c. characterizations revealed the presence of a low molecular weight peak in the PEEK mass distribution (*Figure 3*). Oligomers are known to be frequently rejected when a polymer crystallizes from solution[21]; this leads to the formation of oligomer crystals which melt below the polymer thermodynamic melting temperature. However they could more easily crystallize from the melt than the pure PEEK polymer, because the entanglement constraints are lower for short chain length molecules. Melting the synthesis polymer powder would initially lead to locally high oligomer concentrations in the melt, resulting from oligomer crystals melting. Crystalline oligomer nucleus formation would then be easy. As melt t_{hold} proceeds, these oligomers would diffuse slowly, so that their local concentration would decrease; this would decrease their ability to quickly form nuclei and reduce the overall crystallization kinetics. This hypothesis seems plausible since typical lamellar thicknesses[1] of PEEK crystallized from the molten or amorphous states are of the order of 2–6 nm, i.e. one to four PEEK repeat units per lamellar thickness (based on a lattice parameter along the c-axis of ~ 1 nm)[24–27]. The oligomer g.p.c. peak is around 1750 g mol^{-1}, roughly the 6-mer mass; this suggests that oligomer crystals could be thick enough to act as polymer crystallization seeds.

In summary, the crystallization rate decrease of PEEK molten in nitrogen at temperatures between 385°C and 410°C has been shown to be qualitatively similar to the decrease observed after a 440°C melting in nitrogen, which was shown by g.p.c. to be due to a molecular viscosity increase (also t.g.a. indicated that a degradation was effective at 440°C). This led to the conclusion that the PEEK degradation was also the mechanism responsible for the T_{cc} and ΔH_{cc} decrease for T_{hold} values of <440°C. However, to be complete, it was also mentioned that the T_{cc} decrease could also partly be due to a seed destruction mechanism. Such a mechanism results from an ordered crystalline area surviving up to the thermodynamic melting temperature when $T_{hold} < T_m^0$; when $T_{hold} > T_m^0$, it could consist of the progressive irreversible melting of PEEK crystals initially grown from solution on foreign heterogeneities or of the slow disappearance (through diffusion) of zones of high concentration of faster melt-crystallizing oligomers.

Isothermal crystallizations are another way of evaluating crystallization kinetics. The method is logically equivalent to a non-isothermal technique in view of the conclusions inferred but is more time-consuming and perhaps even less precise because of the d.s.c. cell stabilization time involved at the beginning of the isotherms. However, to check that the same results can be obtained with both methods, and to eventually perform an Avrami analysis, it was decided to record some isothermal crystallizations after various melting conditions in nitrogen: 385°C for 5 min, 400°C for 5 min and 410°C for 15 min. *Figure 15* is a plot of $t_{1/2}$ as a function of T_c for the three melting conditions. It can be seen that the crystallization is faster after 5 min melting at 385°C than after 5 min at 400°C, which is still faster than after 15 min at 410°C. These are exactly the same observations as before.

Avrami analyses were performed because they are frequently given for PEEK in the literature. To ensure that the crystallization exotherms are not perturbed by the initial d.s.c. instability, a low degree of supercooling was chosen ($T_c = 325$°C). *Figure 16* gives the Avrami plot obtained for the three melting conditions, while *Table 7* gives the Avrami coefficients obtained by fitting the evolution of relative crystallinity with time:

$$\frac{X_c}{X_{c,\max}} = 1 - \exp(-Kt^n)$$

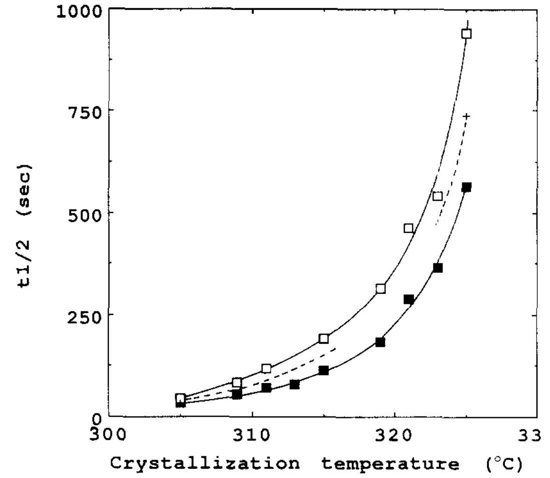

Figure 15 Variation of the PEEK crystallization half-time with crystallization temperature. Melt holding conditions: ■, 385°C for 5 min; +, 400°C for 5 min; □, 410°C for 15 min

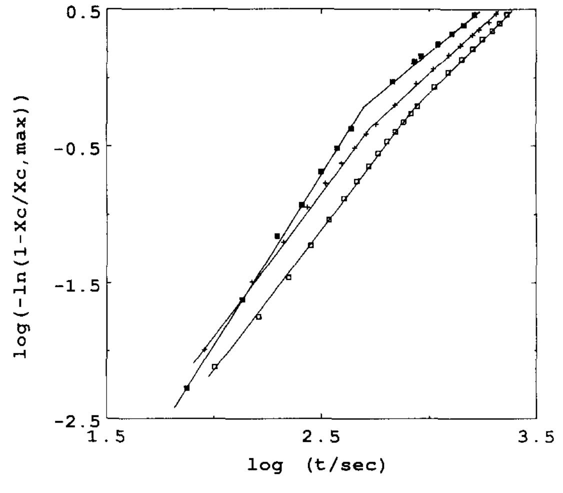

Figure 16 Avrami plots for the PEEK crystallization at 325°C. Melt holding conditions: ■, 385°C for 5 min; +, 400°C for 5 min; □, 410°C for 15 min

Table 7 Crystallization half-time and Avrami coefficients of PEEK molten during t_{hold} at T_{hold} and crystallized at 325°C

T_{hold} (°C)	t_{hold} (min)	$t_{1/2}$ (s)	n_1	n_2	K_1 (s^{-n_1})	K_2 (s^{-n_2})
385	5	565	2.49	1.25	1.19×10^{-7}	2.75×10^{-4}
400	5	737	2.07	1.40	9.89×10^{-7}	6.67×10^{-5}
410	15	943	2.08	1.57	4.97×10^{-7}	1.47×10^{-5}

where X_c is the crystallinity at time t, $X_{c,\max}$ is the crystallinity of the polymer at the end of the crystallization, and K and n are Avrami constants. As mentioned elsewhere[10,11,13,28], the crystallization kinetics process levels off and the complete crystallization process is fitted by two successive different Avrami equations; the levelling off occurs at ~40% relative crystallinity here. The Avrami exponent n_1 obtained for short crystallization times decreases from 2.5 to 2 when T_{hold} is increased from 385 to 410°C. However, the absolute value of this coefficient is quite low, and can apparently hardly be related to any physical meaning. This point will be discussed further.

DISCUSSION

The PEEK degradation mechanism will be discussed and then the self-nucleation behaviour of PEEK will be briefly reviewed. Finally some comments will be made about the isothermal crystallization results.

Thermal degradation

From the above results, it can be said that processing the PEEK automatically leads to its degradation, even in careful processing conditions.

The degradation consists in a progressive branching leading to crosslinking, which is apparent through a M_w and M_z increase with M_n remaining constant. The branching mechanism in nitrogen is slow: only a 10% increase in M_z could be observed after 30 min melting at 440°C. On the contrary, the branching mechanism is very rapid in air: with M_z increases of >10% after 15 min melting at only 385°C, and of nearly 30% after 30 min melting at 400°C. For stronger melt holding conditions, a few per cent of insolubles appear in the polymer. The branching rate in air is related to the oxygen diffusion from the surface into the sample: the volatile emission is linked more to the sample surface than to the sample volume, and the molecular weights are functions of the sample surface to volume ratio.

The branching process results in a molecular viscosity increase, causing a reduction in the crystallization kinetics, and in the introduction of defects along the chain that decreases the crystallinity. One can find for instance in *Table 8* the T_{cc} decrease and the end-of-run crystallinity reduction (calculated assuming 130 J g^{-1} for the melting enthalpy of the 100% crystalline polymer[1]), associated with a 30 min melting at various temperatures in nitrogen (cf. *Figure 14*). A crystallinity rate deterioration can be observed to occur in nitrogen for temperatures very near the melting temperature, and for t_{hold} values of the order of a few tens of minutes only. In air, the crystallinity rate decrease is much more rapid: after 30 min melting at 420°C, the T_c decreases by >30°C.

Volatiles are produced during the degradation process. However, degradation can already be observed through a reduction in ΔH_{cc} though the emission of volatiles is too weak to be detected by t.g.a. For instance we found a reduction in the PEEK crystallization enthalpy of 10% after a t_{hold} of 1 h in nitrogen at 400°C, but no volatile emission could be recorded for such a short time. Clearly the thermal stability of PEEK cannot be assessed only by t.g.a.; mechanical properties of PEEK will certainly be affected by the degradation process, even though no weight loss can be observed with t.g.a.

The branching process thus directly affects the polymer morphology and crystalline content and ultimately the mechanical properties. Note that volatiles production can also be a source of mechanical properties reduction because the introduction of microporosity in the sample can play a role in the crack initiation process. To keep the degradation as low as possible, one has to work in an inert atmosphere, or to use a very low surface to volume ratio geometry in air (i.e. not prepregs). If the polymer morphology has to be well controlled, it would be preferable to process the polymer at temperatures of >385°C to suppress self-nucleation. Furthermore, processing at too low temperatures increases the melt viscosity which can be a hindering factor. Because the degradation rate increases with the melt processing temperature, it would be a good practice to process PEEK at around 400°C to limit degradation while suppressing self-nucleation. The polymer can be held at such a temperature in an inert atmosphere for 30 min without significant decreases in the crystallization rate or in the attainable crystallinity. In air however, the time should be kept as short as possible, because the degradation is very rapid.

Nonetheless if one attempts to compare precisely the crystallization kinetics of PEEK in various conditions (as for example in the presence or absence of carbon fibres, or as a function of the carbon fibre type, and so on), a special emphasis must be placed on keeping the processing conditions totally identical from one sample to another. This is an arduous requirement but absolutely necessary to ensure valid results. Moreover the ideal d.s.c. melt conditions before recording the crystallization are poorly defined because degradation is already effective at temperatures above which self-nucleation is suppressed. An acceptable melting condition prior to recording the PEEK crystallization kinetics seems to be 400°C for 5 min, provided the calorimeter has been totally purged of air.

The influence of PEEK degradation in the usual processing melt conditions under nitrogen, on its crystallization kinetics, has only been recently recognized. Lee and Porter[10], although they noted that a PEEK sample heated at 400°C for 4 h showed an increase in reduced viscosity and was not totally soluble in H_2SO_4, stated that PEEK degradation may indeed occur but at too little an extent to influence their d.s.c. results. They

Table 8 Crystallization temperature decrease and end-of-run weight crystallinity (W_c) reduction for PEEK held at various temperatures for ~30 min in nitrogen. Data from *Figure 14*

T_{hold} (°C)	$T_{cc,\max}$ decrease (°C)	W_c decrease (wt%)
385	1.5	1.3
400	3	1.5
410	4.5	2.2
440	12	6

attributed the crystallization kinetics decrease, observed as a function of the melt t_{hold} at or above 400°C, to the disappearance of remnants of ordered regions and not to the disappearance of crystalline regions grown on foreign heterogeneities or to a degradation mechanism. It was not clearly explained how such remnants could survive during long times at T_{hold} values higher than their assessed thermodynamic melting temperature (389°C). Day *et al.*[11] have reported crystallization temperatures (T_{ch}) of PEEK from the amorphous state to be functions of the melt t_{hold} and T_{hold} before quenching (380–420°C up to 120 min). No variation in the T_g could be detected, and the crystallization enthalpy from the amorphous state was found to vary only slightly with the melt conditions. They conclude that in nitrogen the amount of crystallizable material remains relatively constant with increasing temperature up to 420°C and t_{hold} up to 120 min. Clearly, their results are compatible with the results of the present study: the increase of T_{ch} from the amorphous state, with the holding conditions, parallels the decrease of the T_{cc} with these same conditions. No important variation of the crystallization enthalpy from the amorphous state has been observed because it depends on the segmental molecular mobility close to T_g, which is less branching sensitive as the melt molecular mobility.

PEEK degradation in an oxidative environment has been recognized by various authors. Chan and Venkatraman[29] detected a slow increase with time in the melt viscosity of neat PEEK as the polymer was held at 385°C in air. Cebe[30] observed that upon 24 h annealing of a PEEK film at 319°C in air, an insoluble fraction appeared, apparently correlated to the amorphous fraction of the sample. These observations were thought to be due to crosslinking. The d.s.c. results obtained by Day *et al.*[11] showed a strong decrease in the crystallization kinetics with T_{hold} or t_{hold} in air. The decrease in the crystallization kinetics was attributed to a decrease in the number of nucleation sites due to crosslinking. There is no clear reason however why these authors suppose that the crystallization rate decrease is only due to a decrease in the nucleation rate; the crystallization rate decrease is also related to a lower crystalline growth rate due to the increase in the entanglement density or to real chemical crosslinks caused by the branching process.

These published PEEK crystallization results agree thus with the degradation picture that was developed above. What kind of degradation mechanism would it be possible to postulate to explain this degradation picture? One can suggest that the degradation mechanism consists of a homolytic random chain scission process, producing radicals that attack near polymer chains to form branches and finally crosslinks. The lifetime of these radicals must be high enough to permit the branching reaction before termination (radical deactivation) or unzipping of the radical, since no decrease in M_n has been observed. Volatile emission will then only occur after a scission very near a chain end and only if the produced radical does not undertake a side chain attack on another near macromolecule. This explains why PEEK degradation occurs first without any measurable volatile emission, as for $T_{hold} < 420°C$ and $t_{hold} < 1$ h in nitrogen. This confirms that t.g.a. is not able to elucidate the PEEK degradation process alone.

Day *et al.*[14] have suggested from t.g.a. analysis alone that pyrolysis of PEEK in nitrogen is a random chain scission process. They evaluated the E_a using various procedures, leading to different values from 198 to 236 kJ mol^{-1}. However their study was mainly concerned with T_{hold} and t_{hold} ranges where the degradation is quite important, i.e. well outside the usual melt processing conditions. From their data, they extrapolated that it would be necessary to hold PEEK for at least 100 h at 400°C before recording a weight loss of 5%. The results of the present study suggest that after 100 h melting at 400°C in nitrogen, PEEK would be at least fully crosslinked, and its mechanical properties would be totally changed. This again illustrates the inadequacy of t.g.a. to assess the PEEK thermal stability.

Non-isothermal t.g.a. under air at different heating rates led these authors to the conclusion that in air the controlling mechanism is the transport of oxygen through the melt. Using various procedures to interpret their results, they found in air an E_a of the order of 100–150 kJ mol^{-1} for the first stage of the degradation process, which is comparable to the apparent E_as calculated above.

Volatilization products of PEEK under nitrogen between 430°C and 530°C have been analysed by Hay and Kemmish[13] with g.p.c. and mass spectroscopy. A major degradation product was phenol but they also found many low molecular weight chain fragments with minor structural alterations deriving from PEEK chain scission. The authors found conflicting evidence about which of the links, ether or carbonyl, is the more stable. The E_a for the PEEK degradation was found to be 310 ± 50 kJ mol^{-1}. They suggest the degradation mechanism to be a random homolytic chain scission, producing relatively stable radicals that do not depolymerize. Termination was thought to be due to a transfer mechanism (hydrogen abstraction producing hydroxyl chain ends) or to a combination mechanism producing branchings. The results of the present study invalidates the termination through hydrogen abstraction; at least this termination is far less probable than the reaction leading to crosslinking.

PEEK decomposition volatiles in air were identified using mass spectroscopy by Prime and Seferis[12] to consist mainly of phenol, diphenyl ether, benzophenone and benzoquinone, evolved during t.g.a. heating scans up to 700°C. Degradation was shown to be strongly increased by the presence of copper. These authors determined a weight loss E_a of ~ 100 kJ mol^{-1} for PEEK in air but they stated that more than one decomposition process is involved in the phenomenon. This is in accordance with our own findings, since we found an E_a of ~ 105 kJ mol^{-1}.

All these previous results clearly support the chemical degradation mechanism postulated above. More insight into this mechanism could probably be gained by kinetic degradation studies on very low molecular weight PEEK oligomers.

Self-nucleation

Various T_m^0 have been reported in the literature (395°C[1], 389°C[31], >365°C[32]), based on lamellar thickness *versus* melting temperature or T_c *versus* melting temperature measurements.

Nguyen and Ishida[33] have shown using Fourier transform infra-red spectroscopy that local order is still present in PEEK quenched after 10 min melting at 380°C but is no longer detectable after 10 min melting at 400°C. Lee and Porter[10] have discussed in detail self-nucleation in PEEK. They found a rapid decrease in the crystallization kinetics with the melt T_{hold} up to 390°C, which they attributed to self-nucleation. The optical microscopy results given above showed that crystalline remnants were destroyed by heating the polymer for 5 min between 385°C and 400°C. The convergence of all these results is clear. It seems thus highly improbable that crystalline remnants could survive in sufficient number at temperatures above 400°C, for times longer than a few minutes, except perhaps when adsorbed on foreign substrates.

This is not the conclusion drawn by Kumar *et al.*[9] on the basis of an optical microscope study. These authors measured the PEEK nucleation rate as a function of the melt conditions (380–420°C for 5 min in air), by counting the number of spherulites per unit surface of the sample, viewed between crossed polars in a microscope unit. They found an exponential decrease in the nucleation density with the melt temperature from 380 to 420°C. They suggested that self-nucleation could account for their results or that the presence in PEEK of some other species of the poly(aryl ether ketone) family could explain such a continuous decrease. It has indeed been shown[34] that various specimens of this family are isomorphic, and melting points ranging from 324 up to 391°C have been reported, suggesting that identical ranges exist for the thermodynamic melting temperatures. This hypothesis cannot be a priori discarded, but it remains to be shown how such species could be formed during the polycondensation process. Their experiments were performed in air, so that the decrease of the measured number of spherulites with the increase in T_{hold} results more probably simply from a higher degradation rate, which reduces the nucleation rate through an increase in the molecular viscosity.

Isothermal crystallizations

Isothermal PEEK crystallization from the melt and subsequent Avrami analysis have been performed by various authors[10,11,28,35,36]. It is difficult to compare the $t_{1/2}$ values of this study to the previously published values because the polymer molecular distributions are seldom given in the previous publications. There is however a relation between the crystallization rate and the molecular weight; moreover the presence of oligomers in the distribution can more or less affect the overall crystallization rate. Strong variations in the literature between the melt conditions prior to crystallization result in a supplementary variability.

When comparing their Avrami coefficients results together and with the above results, for low supercoolings, some questions arise: (1) Why do the published PEEK n_1 values range from 2 to 3.8? What is the meaning of a n_1 value ($=2$) when optical microscopy reveals that the PEEK growth is spherulitic in nature? (2) Is the n_1 decrease with crystallization time due to crystalline perfection?

The large range of published n_1 values could be partially explained by various reasons: the crystallization isotherms have been performed by some authors[11,28,35] using Dupont DSC, which are not truly isothermal systems. This can affect the results obtained for high crystallization rates but is not likely to change the results obtained at low supercoolings. Then, the choice of the crystallization starting point ($t=0$) influences[37] the calculated n_1. This choice is not always explicitly stated. Moreover, a frequently met d.s.c. instability at the beginning of the crystallization process, even affecting only weakly the overall crystallization isotherm, can change the n_1 value by $>10\%$. This is shown in *Figure 17*. Starting from the measured crystallization isotherm of PEEK at 325°C after 5 min melting at 400°C (curve a), the beginning of the crystallization process is weakly modified by cutting it arbitrarily but slightly to simulate the effect of an imaginary d.s.c. instability (curves b and c). The corresponding Avrami plots for n_1 ($1\% < X_c < 35\%$) are given in *Figure 17b*; it is seen that a very slight change in the beginning of the exotherm modifies the Avrami plot appreciably and the resulting n_1 decreases from 2 to 1.8.

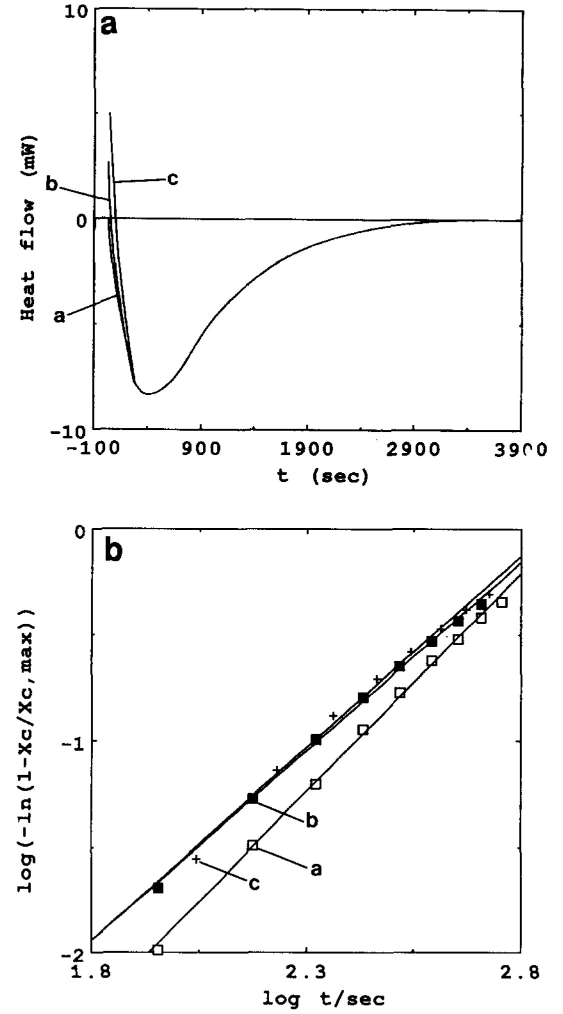

Figure 17 (a) Crystallization isotherm of PEEK crystallized at 325°C after 400°C for 5 min melting (curve a). Curves b and c are obtained from curve a by arbitrarily but slightly cutting it to simulate the effect of a d.s.c. instability. The corresponding Avrami plots are reported in (b)

These considerations throw doubt on the efficiency of an Avrami analysis as a useful tool to scrutinize the crystallization of a polymer such as PEEK. Moreover, whatever the value obtained for n_1, it is practically always possible to find an explanation for the obtained value. It has in fact been stated[21] that without the parallel knowledge of the microscopic independently proven mechanism, an Avrami analysis could not be considered as anything other than a convenient way to represent empirical crystallization data. This is *per se* already an answer to the second part of the first question. To explain for instance that n_1 is around 2 in the above data, an athermal cylindrical growth of PEEK for short crystallization times of the crystallization process could be invoked. This would actually be possible, since it has been suggested[8] from scanning electron microscopy (SEM) observations that bulk PEEK crystalline growth occurs through the development of a lamellar sheaf into a lamella cartwheel (cylinder), prior to development into a three-dimensional spherulitic structure. Such cylindrical lamella cartwheels have also been observed with transmission electron microscopy by other investigators[38] but for PEEK crystallized in thin films. The above Avrami results are not however to be considered as proof of the validity of the postulated growth mechanism.

Finally, in the light of the previous comments, the variation of n_1 with the holding conditions is not considered to be significant.

A decrease in the PEEK crystallization kinetics after a certain time has been observed in this study and also by many authors[10,11,28,35]. Such a slowing down in the crystallization kinetics after the initial crystal growth has been found for various other polymers; it has generally been attributed to secondary crystallization. Secondary crystallization is commonly thought to consist in crystal perfection or in the crystallization of initially hindered or rejected macromolecular segments. Crystalline perfection (lamellar thickening) is known to be present for PEEK held isothermally at high temperature[39] (see also Table 1 of ref. 31 where a logarithmic increase in crystallinity with t_{hold} can be observed at 269.3°C). Such crystalline perfection has been shown for instance to be the reason of the fast decrease in the Avrami exponent of poly(ethylene oxide)[40]. Some authors[28,35,41–43] have recently suggested from SEM and d.s.c. results that two lamella populations would be formed during the PEEK crystallization; these populations differing from the other with respect to their lamellar thicknesses. The first population lamella, the dominant lamella, would be thicker and formed first, whereas the second, subsidiary lamella, would be thinner and would appear later. This has been invoked to explain the double melting behaviour of PEEK. This could explain also the two-stage crystalline growth in PEEK. However, this approach has been severely criticized by Blundell[39] on the basis of lamellar thickness measurements and another interpretation of the double-melting behaviour of PEEK has been given by Lee and Porter[31] as due to recrystallization during the d.s.c. heating scans. With the present state of affairs, it is difficult to assign precisely a given mechanism for the slowing down of the PEEK crystallization kinetics.

CONCLUSIONS

PEEK thermal stability in air and in nitrogen, at usual melt processing temperatures, has been assessed. A branching mechanism, leading to crosslinking, has been shown by g.p.c. to occur in PEEK held in the molten state in air. In nitrogen the degradation mechanism is much weaker, although detectable.

A random homolytic chain scission has been postulated to be the first step of the degradation mechanism. The produced radicals have sufficient stability, so that unzipping or radical deactivation does not occur before the second step of the degradation mechanism, which consists in branching reactions. Volatiles emission can be observed only after scission occurring near a chain end. Since this is a less probable event, the volatiles emission is easily detected only after the degradation has already significantly proceeded. It has been therefore suggested that t.g.a. is not a convenient means to assess PEEK degradation.

PEEK degradation has been shown to decrease considerably the polymer crystallization kinetics, through an increase in the molecular viscosity. The final crystallinity obtained is also decreased by degradation; it has thus to be expected that the PEEK structural properties, which are morphology dependent, are also affected by the melt holding conditions. A convenient processing condition to reduce the branching mechanism as much as possible is suggested to be 400°C for <30 min in an inert atmosphere. If processing is done in air, one has to be aware that the polymer will progressively branch, especially when processing high surface to volume ratio samples.

There are no ideal melt conditions before recording a crystallization thermogram for PEEK. Degradation is already present at temperatures where self-nucleation is not yet suppressed (385°C). Degradation could be minimized, however, if one melts the polymer for 5 min at 400°C in nitrogen; for such a melt condition, self-nucleation will be also suppressed. However, it was impossible to confirm that some very special kind of thermally deactivated nucleants could not be still active after such a melting condition. Two possible examples of such nucleants were given, namely crystalline zones stabilized on foreign heterogeneities or local concentrations of more mobile oligomers.

Finally, some criticism was formulated concerning the frequent use of Avrami plots to elucidate the PEEK crystallization mechanism.

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REFERENCES

1 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953
2 Nguyen, H. X. and Ishida, H. *Polym. Comp.* 1987, **8**, 57
3 Reilly, J. J., Thoman, S. J. and Lin, W. W. 18th Int. SAMPE Tech. Conf. 1986, **18**, 22
4 Kemmish, D. J. and Hay, J. N. *Polymer* 1985, **26**, 905
5 Grayson, M. A. and Wolf, C. J. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 31
6 Mensitieri, G., Apicella, A., Kenny, J. M. and Nicolais, L. *J. Appl. Polym. Sci.* 1989, **37**, 381
7 Cattanach, J. B. and Cogswell, F. N. in 'Developments in Reinforced Plastics' (Ed. G. Pritchard), Vol. 5, Elsevier, London, 1986
8 Blundell, D. J., Crick, R. A., Fife, B., Peacock, J., Keller, A. and Waddon, A. *J. Mater. Sci.* 1989, **24**, 2057
9 Kumar, S., Anderson, D. P. and Adams, W. W. *Polymer* 1986, **27**, 329
10 Lee, Y. and Porter, R. S. *Macromolecules* 1988, **21**, 2770
11 Day, M., Suprunchuk, T., Cooney, J. D. and Wiles, D. M. *J. Appl. Polym. Sci.* 1988, **36**, 1097
12 Prime, R. B. and Seferis, J. C. *J. Polym. Sci., Polym. Lett. Edn* 1986, **24**, 641
13 Hay, J. N. and Kemmish, D. J. *Polymer* 1987, **28**, 2047
14 Day, M., Cooney, J. D. and Wiles, D. M. *J. Appl. Polym. Sci.* 1989, **38**, 323

15 Daoust, D., Devaux, J. and Legras, R. to be published
16 Devaux, J., Delimoy, D., Daoust, D., Legras, R., Mercier, J.-P., Strazielle, C. and Nield, E. *Polymer* 1985, **26**, 1994
17 Devaux, J., Daoust, D., Legras, R., Dereppe, J. M. and Nield, E. *Polymer* 1989, **30**, 161
18 Attwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, L. R. J., Rose, J. B. and Staniland, P. A. *Polymer* 1981, **22**, 1096
19 Legras, R., Leblanc, D., Daoust, D., Devaux, J. and Nield, E. *Polymer* 1990, **31**, 1429
20 Jonas, A., Lemaire, K. and Legras, R. to be published
21 Wunderlich, B. 'Macromolecular Physics, Vol. II. Crystal Nucleation, Growth, Annealing', Academic Press, New York, 1976
22 Binsbergen, F. L. in 'Progress in Solid State Chemistry' (Eds J. O. McCaldin and G. Somorjai), Vol. 8, Pergamon Press, Oxford, 1973; and references therein
23 Turnbull, D. *J. Chem. Phys.* 1950, **18**, 198
24 Dawson, P. C. and Blundell, D. J. *Polymer* 1980, **21**, 577
25 Rueda, D. R., Ania, F., Richardson, A., Ward, I. M. and Balta Calleja, F. J. *Polym. Commun.* 1983, **24**, 258
26 Hay, J. N., Kemmish, D. J., Langford, J. I. and Rae, A. I. M. *Polym. Commun.* 1984, **25**, 175
27 Fratini, A. V., Cross, E. M., Whitaker, R. B. and Adams, W. W. *Polymer* 1986, **27**, 861
28 Cebe, P. and Hong, S. D. *Polymer* 1986, **27**, 1183
29 Chan, C. M. and Venkatraman, S. *J. Appl. Polym. Sci.* 1986, **32**, 5933
30 Cebe, P. *J. Mater. Sci.* 1988, **23**, 3721
31 Lee, Y. and Porter, R. S. *Macromolecules* 1987, **20**, 1336
32 Khanna, Y. P. and Kumar, R. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 369
33 Nguyen, H. X. and Ishida, H. *Polymer* 1986, **27**, 1400
34 Harris, J. E. and Robeson, L. M. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 311
35 Velisaris, C. N. and Seferis, J. C. *Polym. Eng. Sci.* 1986, **26**, 1574
36 Jog, J. P. and Nadkarni, V. M. *J. Appl. Polym. Sci.* 1986, **32**, 3317
37 Tomka, J. *Eur. Polym. J.* 1968, **4**, 237
38 Lovinger, A. J. and Davis, D. D. *J. Appl. Phys.* 1985, **58**, 2843
39 Blundell, D. J. *Polymer* 1987, **28**, 2248
40 Kovacs, A. J. and Gonthier, A. *Kolloid Z. Z. Polym.* 1972, **250**, 530
41 Cebe, P. *Polym. Eng. Sci.* 1988, **28**, 1192
42 Cheng, S. Z. D., Cao, M.-Y. and Wunderlich, B. *Macromolecules* 1986, **19**, 1868
43 Bassett, D. C., Olley, R. H. and Al Raheil, I. A. M. *Polymer* 1988, **29**, 1745