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Effects of Thermal History on Crystallization of Poly(ether ether ketone) (PEEK)

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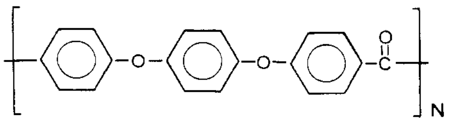
ABSTRACT: The crystallization of poly(ether ether ketone) (PEEK) has been investigated as a function of thermal history. Isothermal (315, 311 °C) and nonisothermal crystallizations of two reactor powders and one film have been conducted by differential scanning calorimetry (DSC). Isothermal crystallizations at 315 °C have been analyzed by using the Avrami equation. As the temperature in the melt was increased, the Avrami exponent (n) slightly increased (from 3.4 to 3.8), but the parameter k decreased and the crystallization exotherms on cooling (−10 °C/min) shifted to lower temperatures. As the holding time in the melt was increased, the isothermal crystallization curves shifted to longer time. These observations are consistent with a persistence of small residual crystalline regions in the bulk. When the melt of PEEK has been held at or above 390 °C, the subsequent crystallization behavior (isothermal as well as nonisothermal) is nearly independent of the prior melt temperature. It is thus proposed that the residual crystalline regions only persist up to the thermodynamic melting point. Several semicrystalline polymers, including PEEK, support this description. The thermal stability at the melt temperatures has been assessed by thermogravimetric analysis (TGA) and by solution viscosity.

Introduction

Considerable attention has been given to poly(ether ether ketone) (PEEK) as a high performance thermoplastic, as well as a matrix for advanced composites.[1-5] The repeat unit of PEEK is



Its glass transition temperature (T_g) is ~143 °C, its common melting temperature ~334 °C, and its crystallinity is 0–48%, depending on sample history.[6] Alterations in crystallization conditions are known to result in different crystal morphologies, which influence product properties.

It has been known that the thermal history in the melt or solution affects the crystallization behavior of many polymers.[7] Therefore, the thermal history prior to crystallization must be treated carefully, as well as other crystallization conditions. As the melt temperature is increased, the number of nuclei decreases and, therefore, overall crystallization rate decreases. Reported examples are polyethylene,[8] isotactic polypropylene,[9] isotactic polystyrene,[10] poly(chlorotrifluoroethylene),[11,12] nylon 6,[13] nylon 6,6,[14] poly(ethylene oxide),[15,16] poly(oxymethylene),[17] and poly(ethylene terephthalate).[18,19] Unlike solution crystallization,[20,21] the holding time in the melt also influences the crystallization of polymers.[13,14,17] However, contradictory results have been also obtained for polyethylene[22] and poly(decamethylene terephthalate);[23] crystallizations of the polymers were found to be independent of the previous melt temperature.

It has been noted that crystallization of PEEK in composites depends on melt temperature (melt-annealing temperature) and holding time in the melt (melt-annealing

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Table I
Viscosities, Number- and Weight-Average Molecular Weights ($\bar{M}_n$ and $\bar{M}_w$, Respectively), Onset Temperature of Degradation, and Ash Content of Three PEEK Samples

	viscosity					
sample code	melt,[a] N s m^{-2}	soln,[b] dL g^{-1}	$\bar{M}_n$,[c] g mol^{-1}	$\bar{M}_w$,[c] g mol^{-1}	onset of[d] degradatn °C	ash content, %
powder I	380	0.94	14 100	38 600	570.3	0.4
powder II	450	0.99	16 800	39 800	578.2	0.1
film		0.70			554.1	0.4

[a] At shear rate of 1000 s^{-1} at 400 °C, provided by ICI. [b] Reduced solution viscosity. [c] Provided by ICI. [d] From weight loss curves.

time).[3,24,25] A cumulative effect of melt annealing has also been found for PEEK and successfully used in the nucleation density measurement of PEEK in carbon fiber composites.[3] A more extended study on the effects of melt-annealing temperature and time on crystallization of PEEK is reported here.

Experimental Section

Two PEEK reactor powders of different molecular weights and an amorphous PEEK film were obtained from Imperial Chemical Industries (ICI, Wilton, U.K.) and Westlake Plastics Co. (Lenni, PA), respectively. Melt and solution viscosities, average molecular weights, onset temperature of degradation, and ash content of the samples are listed in Table I. The reduced solution viscosities were measured at 25 °C in 98% sulfuric acid at a concentration of 0.1 g/dL by using an Ubbelohde type viscometer. Since dissolution and sulfonation of PEEK occur concurrently in sulfuric acid,[26] the duration time before viscosity measurement was kept constant (15 h).

Thermogravimetric analysis has been conducted with a Perkin-Elmer TGS-2 under nitrogen atmosphere. Weight loss curves were obtained at a heating rate of 5 °C/min and nitrogen flow rate of 50 cm^3/min. Temperature was calibrated with the Curie points of nickel, perkalloy, and iron. The onset temperature of degradation is defined by the temperature where the tangent to the curve at its maximum negative slope intercepts the original zero-slope tangent.[27] Ash content was measured by the University of Massachusetts Microanalysis Laboratory. Sample weights were measured before and after oxidation at 900 °C under oxygen atmosphere for 3 h. Number- and weight-average molecular weight and melt viscosity of the PEEK powder samples were provided by ICI. All the samples were vacuum-dried at 145 °C overnight prior to use. PEEK powder was screened out by using a mesh (no. 170), and the fine powder (<80 μm) was used in this study. This allowed good thermal contact of the powder with aluminum DSC sample pans.

Crystallizations of PEEK after various thermal histories have been characterized with Perkin-Elmer differential scanning calorimeters (DSC-2 and -4). Isothermal crystallizations at 315 and 311 °C were performed in a DSC after melting PEEK samples at various temperatures (370–420 °C), considerably higher than the commonly observed melting temperature (~334 °C), for several time periods (10–240 min). The rates of cooling from the melt were 320 and 200 °C/min for DSC-2 and DSC-4, respectively. Another set of samples was heated to various melt-annealing temperatures (370–420 °C), held for 30 min, and then cooled at −10 °C/min. The crystallization curves on cooling were recorded.

Temperatures and heats of transition were calibrated with pure metal standards, namely, indium, tin, lead, and zinc for each heating rate. Isothermal crystallization and melt temperatures were calibrated with extrapolated melting points of the standards to zero heating rate. For cooling scans (−10 °C/min) the temperature was calibrated with heating scans of the standards at 10 °C/min since the cooling rate was low. All experiments with a DSC were conducted under dry nitrogen. DSC traces were normalized to 1 mg of sample as shown in the figures.

Results and Discussion

The crystallization behavior of two PEEK powders and one amorphous PEEK film has been studied with differential scanning calorimetry (DSC). Figure 1 shows heating scans (80 °C/min) of the three PEEK samples, as received. The first DSC trace of powder I (trace A) shows a melting endotherm (12.8 cal/g) at 340 °C and a small cold-crystallization exotherm (~1.1 cal/g) at 174 °C. In the second heating scan (trace A′) of the same sample after cooling (−150 °C/min) from 400 °C, the peak temperature of the melting endotherm (10.4 cal/g) decreases to 334 °C, and the cold-crystallization exotherm disappears. This suggests that the PEEK reactor powder may have some special crystalline morphology due to simultaneous polymerization and crystallization during synthesis.[7,28] Similarly, the first heating of powder II (trace B) shows a melting peak at 340 °C and cold-crystallization peak (~0.8 cal/g) at 193 °C. Also the first DSC trace of amorphous film (trace C) shows a melting peak at 333 °C, about 7 deg lower than the reactor powders, and a cold-crystallization exotherm around 185 °C.

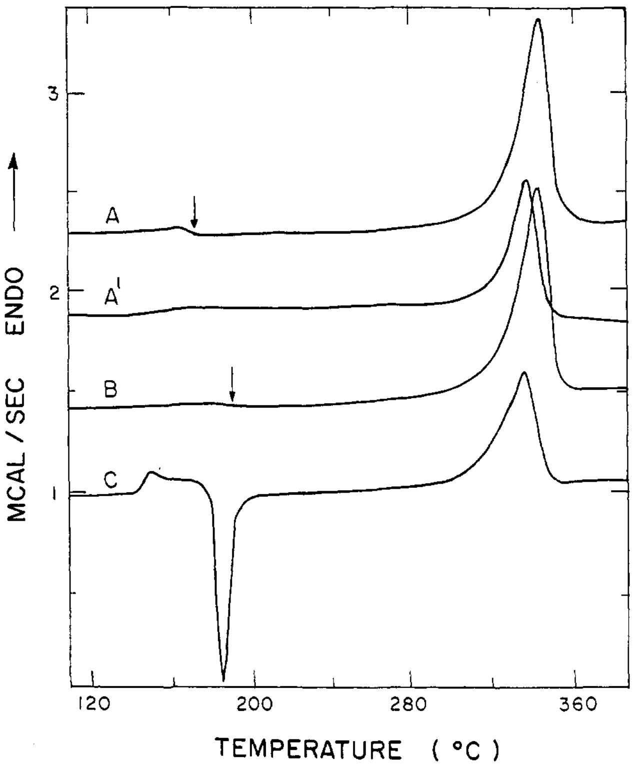

Figure 1. DSC traces of PEEK samples on heating (80 °C/min): A, the first heating of powder I; A′, the second heating of powder I; B, the first heating of powder II; C, the first heating of amorphous PEEK films. Two arrows indicate small cold-crystallization exotherms of powder I and II.

PEEK powder I was isothermally crystallized at 315 °C in a DSC after melting for 10 min at various temperatures (370–410 °C). Subsequent DSC traces are shown in Figure 2. As the melt temperature was increased, the isothermal crystallization curves shifted to longer time and became broad. Also the peak of the curve (t_{peak}, peak crystallization time), i.e., where the maximum crystallization rate is observed, increased. It is notable that the crystallization curves after melting at 390 and 400 °C are almost identical.

The Avrami equation has been widely used to analyze isothermal crystallizations[29,30]

$$\mathrm{Xc}(t)/\mathrm{Xc}(\infty) = 1 - \exp(-kt^n)$$

$$\log\,(-\ln\,(1 - \mathrm{Xc}(t)/\mathrm{Xc}(\infty))) = n \log t + \log k$$

where Xc(t) and Xc(∞) are the crystallinity at time t and the crystallinity at the end of crystallization, respectively. The time, t, was measured from the time when samples were cooled to crystallization temperature. Since determination of the absolute degree of crystallization is not

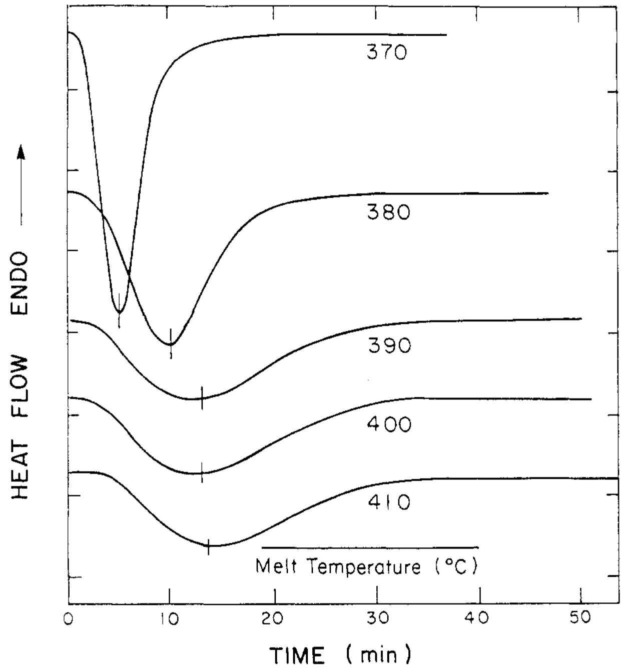

Figure 2. DSC isothermal crystallization curves of PEEK powder I at 315 °C after melting at various temperatures (370–410 °C) for 10 min. Peaks of the curves are indicated by short bars.

Table II
Avrami Parameters (n and k) and Peak Crystallization Time (t_{peak}) for Isothermal Crystallization of Powder I at 315 °C after Melting at Various Temperatures (370–410 °C) for 10 min

melt temp, °C	n	k	t_{peak}, min
370	3.4	2.6×10^{-3}	4.3
380	3.6	1.5×10^{-4}	10.3
390	3.6	6.7×10^{-5}	12.8
400	3.6	4.8×10^{-5}	12.9
410	3.8	2.9×10^{-5}	13.5

required in the Avrami analysis, the ratio of the area at time t and the area of whole exotherm was used for $Xc(t)/Xc(\infty)$.[31,32] The exponent, n, is dependent on the type of nucleation and the crystal growth geometry; the parameter k is also a function of nucleation and growth.

The Avrami parameters n and k are estimated from the slope and intercept respectively in a plot of $\log(-\ln(1 - Xc(t)/Xc(\infty)))$ vs $\log(t)$ as shown in Figure 3. Each curve shows an initial linear portion, subsequently tending to level off. Such leveling off has been also found by Cebe and Hong for PEEK, considered by them to be due to secondary crystallization.[33] The linear portions are almost parallel to each other, shifting to longer time with increasing prior melt temperature. It is notable that crystallization becomes independent of melt temperature for samples previously melted at or above 390 °C. Comparable behavior has also been found for many other polymers, as discussed later. The Avrami parameters n and k, determined from the initial linear portion in Figure 3 and the peak crystallization time (t_{peak}), are listed Table II. As the melt temperature was increased, the exponent n and t_{peak} increased, but k decreased.

For spherulitic growth and athermal nucleation, i.e., all crystals start growing at the same time, the value of n is expected to be 3.[7] In the case of thermal nucleation, i.e., nuclei are created sporadically in time and space, the exponent is expected to be 4. However, complications in the Avrami analysis often arise since several assumptions, which do not necessarily apply to polymer crystallizations, are involved in the derivation.[7] The Avrami exponent (n) showed an increase between 3 and 4 with increasing melt temperature, which may be at least partially, due to the fact that homogeneous nucleation becomes more predominant with increased melt temperature. Hartley et al. found an increase in the exponent n from 3 to 4 for poly(ethylene terephthalate) (PET) when the melt temperature was increased from 268 to 275 or 294 °C.[19] They also found that k decreased with increasing melt temperature which is in agreement with the data in Table II. The changes in n and k for PET were attributed to thermodynamically stable, minute crystals surviving observed melting temperature.[19] It has been previously estimated by Cebe and Hong that $n = 3.3$, $k = 8.0 \times 10^{-5}$, and $t_{peak} = 15.9$ min at 315 °C after melting PEEK film at 400 °C for several minutes.[33] The authors believed that PEEK crystallized heterogeneously by simultaneous nucleation, possibly due to a nucleating agent. Ash (metal oxides) content of the three samples have been measured to be about 0.1–0.4% as shown in Table I. The exponents n in Table II are larger than those previously reported,[33] probably because reactor powder, free from deformation history, was studied here. Deformation of polymer chains can induce nucleation; strain-induced crystallization of PEEK has been reported.[34]

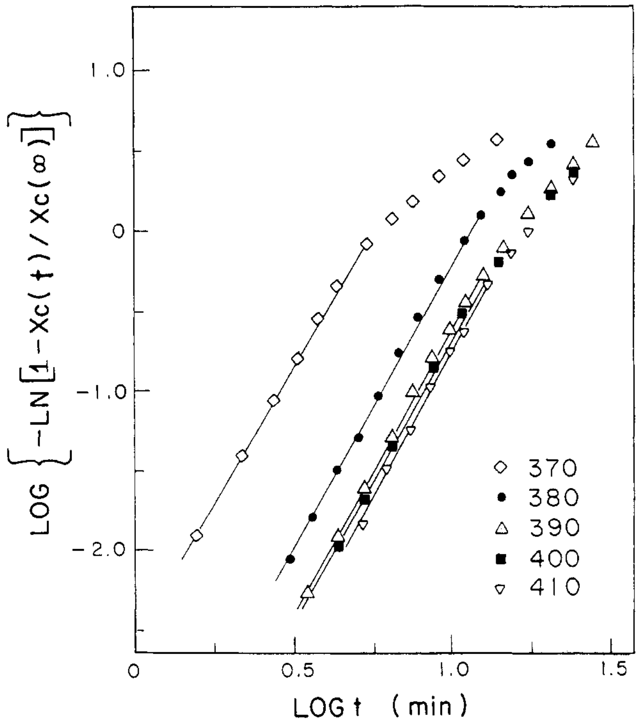

Figure 3. Plot of log (-ln (1 - Xc(t)/Xc(∞))) vs log (time) for isothermal crystallizations shown in Figure 2.

Morgan proposed that residual minute crystalline regions persist above the nominal melting temperature of a polymer.[35] The more perfect the crystalline region, the higher the temperature required for melting. If the melt temperature is not sufficiently high, remnants of former crystals, which might be relatively more ordered, in the melt will act as nuclei for crystallization on subsequent cooling. As the melt temperature is increased, the ordered regions become a homogeneous nonnucleating melt. A polymer usually melts over a wide temperature range due to distributions of crystal size and perfection, molecular weight, and sample history. Along these lines, Wunderlich has proposed that residual annealed high-molecular-weight crystals are likely to survive the observed bulk melting temperature and to self-nucleate.[7] The coined term self-nucleation has been used to describe nucleation of a

Table III
Maximum Temperatures for Self-Nucleation[7] and Thermodynamic Melting Point of Various Polymers

polymer	max temp for self-nucleation, °C	thermodynamic melting point,[a] °C
polystyrene	230[40]	235–250
poly(ethylene terephthalate)	290[19]	245–284, 290,[41] 310,[42] 340[43]
nylon 6	260[13]	214–250, 260,[44] 278[45]
polyethylene	138.5[38]	137–146
poly(ethylene oxide)	69, 100[38] [b]	62–76
poly-1-butene form I	141[38]	126–142
poly-1-butene form II	130[38]	122–130
polychlorotrifluoroethylene	305[11]	210–222

[a] From the *Polymer Handbook*,[39] otherwise the reference is cited. [b] Showed two critical temperatures.

polymer melt or solution by its own crystals grown previously.[7,36] Nucleation centers attributed to annealed high-molecular-weight crystals have been observed for solution-crystallized polyethylene.[21]

The effects of thermal history on crystallization have also been attributed to the persistence of small crystalline regions trapped in cavities of solid impurities, as suggested by Turnbull.[37] If the crystalline material wets the cavity walls, the crystals in the cracks melt at a higher temperature than the bulk, depending on the curvature and size of the cracks and interfacial tension. Upon cooling, when the bulk of the liquid will supercool, the persistent crystals contained in the impurity cracks will serve as nuclei for crystallization.

The two above explanations are considered to account without conflict for many of the previous observations on the relation between thermal history and crystallization. The number of nuclei in various polymers have been measured as a function of melt temperature. The number of nuclei decreased with increasing prior melt temperature and eventually leveled off to a constant value (10^4–10^6 nuclei/g).[7,38] The nuclei which disappeared upon melting were attributed to self-nucleation, while those which did not disappear were attributed to the nucleation on foreign heterogeneities. The temperature at which the self-nucleation disappears and reported thermodynamic melting points defined as the temperature, at which the infinitively large and perfect crystal melts, are compared in Table III. The two temperatures are close for several polymers with one exception, poly(chlorotrifluoroethylene). The closeness of the two temperatures may suggest that the remnants of previous crystals survive the temperatures up to the thermodynamic melting point.

In Figure 4, isothermal crystallization curves of PEEK powder I at 311 °C after melt annealing at 400 °C for various times are shown. As the melt-annealing time was increased, the crystallization curves shifted to longer time. This time dependency, little of which was observed for solution crystallization,[20,21] can be explained by the high viscosity and chain entanglement in a polymer melt. It may take rather a long time even above the ordinary melting temperature, for the previous crystalline regions in the bulk or in the cracks of the foreign particles, to lose order and become a completely homogeneous melt. This has been supported by the observation that as melt-annealing time at 390 °C was increased, fewer of PEEK spherulites developed at the initial stage upon cooling.[3] It was also found for carbon-fiber-reinforced PEEK that crystallization of PEEK depended on the melt-annealing time.[3,24,25] The heats of crystallization of the curves in Figure 4 are similar (~9.5 cal/g). Avrami analysis was not performed for these isothermal crystallizations at 311 °C because heat flow was too small for the crystallization after melt annealing for long time or at high temperature.

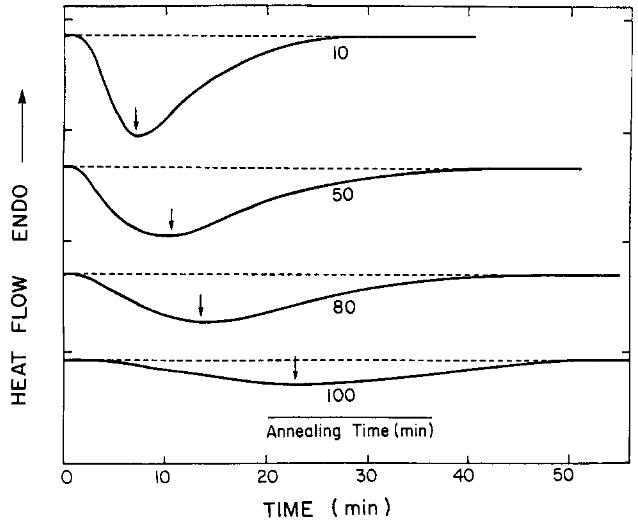

Figure 4. DSC isothermal crystallization curves of PEEK powder I at 311 °C after melting at 400 °C for various time. Peak crystallization times of the curves are indicated by arrows.

A similar study on nylon 6 was previously reported;[46] isothermal crystallization curves were found to shift to longer time as either melt-annealing time or temperature was increased. Also, induction periods, i.e., the time before appreciable crystallization, increased with melt-annealing time and temperature. The authors found an abrupt increase in the induction periods at 280 °C, which is close to the thermodynamic melting point of nylon 6, 278 °C.[46] This was explained by a hypothesis that all residual crystals or ordered regions disappear at the thermodynamic melting point.

In this study on PEEK, it was found that the induction time was technically difficult to determine due to an instrumental electrical overshooting signal, which persists for as long as 2 min. Therefore, the peak of the crystallization curves have been used in Figure 5. The peak crystallization time increases with increases in either melt-annealing temperature or time. At 370 or 380 °C the peak time only slowly increases with melt-annealing time. However, a rapid increase in peak crystallization time is observed for melt temperatures at or above 400 °C. This rapid increase cannot be explained fully by crystalline regions trapped in cavities of solid impurities. It may be due to the disappearance of the remnants of former crystals or ordered regions. Indeed, local order associated with the diphenyl ether moiety has been observed by Fourier transform infrared spectroscopy (FTIR) for PEEK melted at 380 °C, but not for PEEK melted at 400 °C.[47] The authors suggested that the local order persisted up to the thermodynamic melting point of PEEK.

Figure 6 shows the same plot as Figure 5 for an amorphous PEEK film of lower molecular weight. A behavior similar to powder I is observed; peak crystallization time increases rapidly with time when the prior melt temperature is at or above 400 °C. Therefore the rapid increase in peak crystallization time appears to be an inherent property of PEEK. The PEEK film was found to have a little anisotropy due to processing: birefringence of 0.02[48] and c-axis crystal orientation function of 0.07[4] after crystallization. Orientation of polymer molecules often creates many nuclei and, therefore, induces fast crystallization.[34,49] At given thermal history, the PEEK film shows shorter peak crystallization time than powder I, which may be due to the anisotropy and lower molecular weight of the PEEK film.

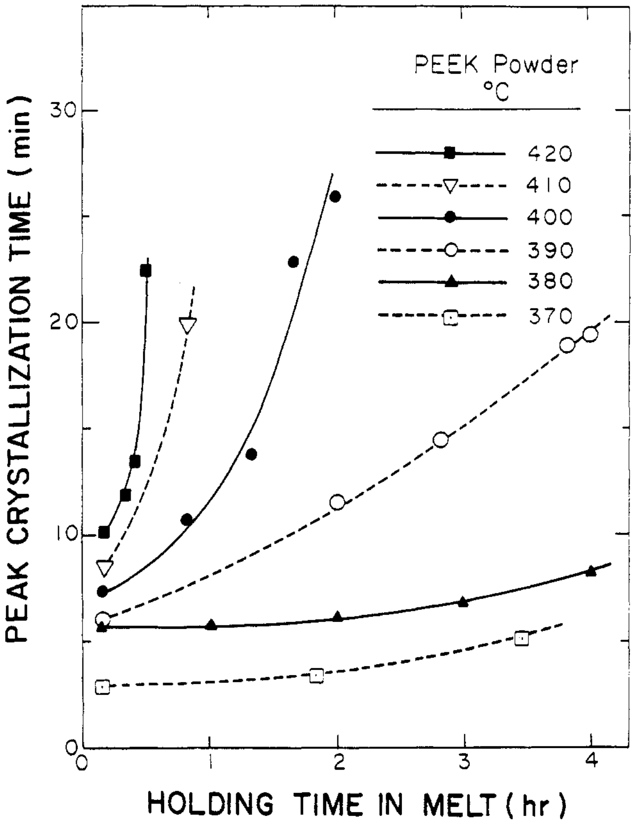

Figure 5. Peak crystallization times of the isothermal crystallization of powder I at 311 °C after melting at various temperature (370–420 °C) for various time.

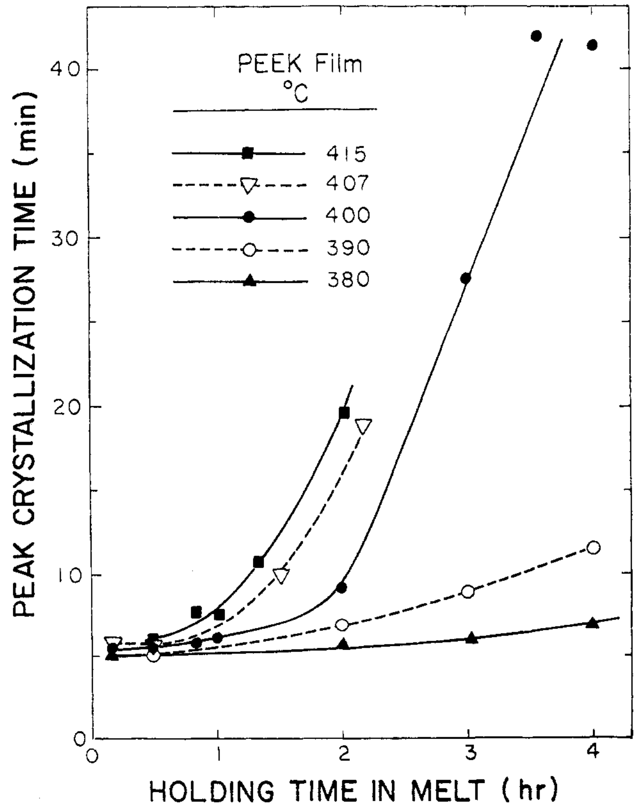

Figure 6. Peak crystallization times of the isothermal crystallization of films at 311 °C after melting at various temperature (380–420 °C) for various time.

PEEK powder I was cooling scanned after being held in the melt for 30 min at various temperatures (370–420 °C). The DSC traces are shown in Figure 7. As melt-annealing temperature was increased, the crystallization exotherm shifted to lower temperatures and became broad. The temperature at which the crystallization exotherm begins is taken as the "onset temperature" where the supercooling is large enough for PEEK to crystallize. The onset and peak temperatures of the crystallization curves are indicated in Figure 7 by short bars. As the melt-annealing temperature was increased, both the onset and peak temperatures decreased. This behavior was also observed for another PEEK powder sample (powder II) and the mixture of powders I and II (20 wt % of powder II).

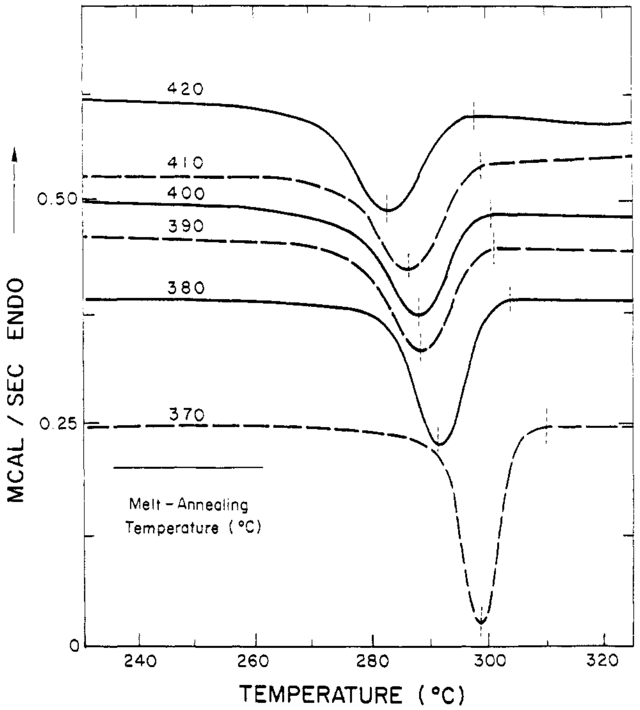

Figure 7. DSC cooling curves (−10 °C/min) for powder I after melting at various temperatures (370–420 °C) for 30 min.

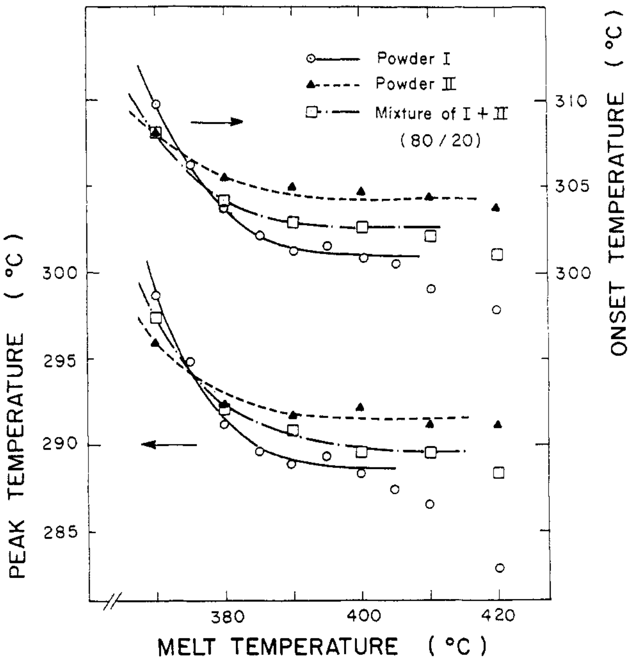

Figure 8. Onset and peak temperatures of DSC cooling curves for powders I and II and their mixture after melting at various temperatures (370–420 °C) for 30 min.

The onset and peak temperatures of the crystallization exotherms for three powder samples are listed in Table

Table IV
Onset (T_{onset}) and Peak Temperatures (T_{peak}) and Heats of Crystallization (ΔH_c) on Cooling (-10 °C/min) of PEEK after Melt Annealing for 30 min at the Temperatures Indicated

	powder I					powder II		mixture I and II[b]	
melt temp, °C	T_{onset}, °C	T_{peak}, °C	ΔH_c, cal/g	ΔH_f,[a] cal/g	T_m,[a] °C	T_{onset}, °C	T_{peak}, °C	T_{onset}, °C	T_{peak}, °C
370	309.8	298.8	10.5	10.4	339.7	308.1	296.0	308.1	297.4
375	306.3	294.9	10.6						
380	303.8	291.3	9.9	9.8	338.5	305.6	292.5	304.1	292.2
385	302.2	289.7	10.1						
390	301.3	288.9	9.5	9.5	337.9	305.0	291.6	303.0	291.0
395	301.6	289.5	9.6						
400	300.9	288.4	9.7	9.6	337.6	304.6	292.3	302.7	289.7
405	300.5	287.5	9.6						
410	299.0	286.6	9.5	9.5	337.2	304.4	291.3	302.2	289.7
420	297.9	282.8	9.4	9.4	336.7	303.8	291.3	301.1	288.5

[a] Heats of fusion (ΔH_f) and peak temperatures (T_m) of melting endotherms (20 °C/min) for powder I crystallized on cooling. [b] 80 wt % powder I and 20 wt % powder II were mixed.

IV and plotted vs the prior melt temperature in Figure 8. Both the onset and peak temperatures were decreased with increased melt temperature. When two melt annealings were performed on a sample at different temperatures, the crystallization behavior was more dependent on the higher melt-annealing temperature. The irreversible dependence on melt-annealing temperature and time has been shown for poly(ethylene terephthalate),[18] nylon 6,[50] and PEEK.[3] Both the onset and peak temperatures leveled off around 390 °C, suggesting that the number of nuclei decreased to be constant on approaching 390 °C. This result as well as the isothermal crystallization data (Figures 3, 5, and 6) indicates that the maximum self-nucleation temperature of PEEK is about 390 °C which is close to the reported thermodynamic melting point, 389 °C[5] and 395 °C.[43]

Powder II, which has a higher molecular weight than powder I, crystallizes at lower temperatures when the melt temperature is below 375 °C as shown in Figure 8. Usually polymers of higher molecular weight show slower crystallization rate due to higher viscosity.[51] However, powder II crystallizes at higher temperatures when melt temperature is above 375 °C. The onset and peak temperatures of powder II are less sensitive to melt temperature than powder I. The mixture of powder I (80%) and powder II (20%) shows the onset and peak temperatures in the middle of the two powder samples (Figure 8). Since the size of the powder is less than 80 μm, powder mixing is expected to be good enough to show the effects of molecular weight. Indeed, the mixture of powders became one piece of film in the aluminum sample pan after melting and crystallization. Considering the smaller portion of powder II in the mixture and the limited mixing, the crystallization of the mixture was more dependent on higher molecular weight fraction. The onset and peak temperature of powder I decreased when the melt temperature was over 400 °C, but those of powder II and the powder mixture did not decrease considerably, suggesting that the decrease is not due to a thermal reaction.

Table IV also shows the heats of crystallization of powder I obtained on cooling. As the melt-annealing temperature was increased to 390 °C, the heat of crystallization slightly decreased. When melt-annealing temperatures were 390–420 °C, almost the same value of heat of crystallization is observed, which suggests that no considerable thermal reactions on PEEK molecules occurred during these melt annealing. The samples crystallized on cooling have been heat-scanned at 20 °C/min. As shown in Table IV, the heat of fusion is almost the same as the heat of crystallization on cooling. The peak temperatures of the melting endotherms decreased gradually with increased melt-annealing temperature, due to the difference in crystallization temperatures on cooling (Figure 7).

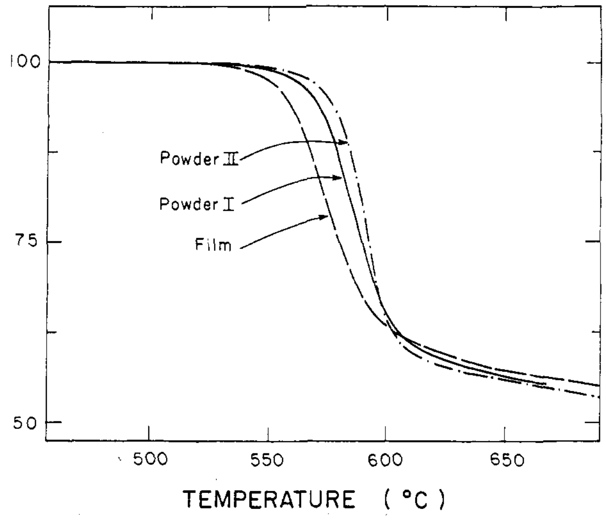

Figure 9. Weight loss curves for PEEK under nitrogen atmosphere (heating rate 5 °C/min).

The thermal stability of the polymer at the melt temperatures was also assessed. Degradation, chain branching, and cross-linking are suspected to occur in PEEK at high melt temperatures. However, the crystallization of PEEK was found to be unaffected by exposure to 375 °C for 4 h under nitrogen atmosphere.[52] Also, the similar values of the heat of crystallization after melt annealing confirms this observation (Table IV). Results of the thermogravimetric analysis of PEEK under nitrogen atmosphere are shown in Figure 9. The onset temperatures of weight loss for the three PEEK samples are well above the melt-annealing temperatures used in this study, as listed in Table I. These data are in agreement with a recent study on the thermal stability of PEEK,[53] where it was found that phenol and benzoquinone are the major decomposition products. PEEK with higher molecular weight shows higher thermal stability as shown in Figure 9. Little change in degradation curves was found for powder I melt annealed at 430 °C up to 2.8 h.

Nonetheless, it has been reported that the viscosity of PEEK measured in air increased with dwell time at 350–380 °C, suggesting that cross-linking occurs.[54] PEEK powder I melt annealed at 400 °C up to 2.5 h under nitrogen atmosphere showed almost the same reduced viscosity (0.94 dL/g) as the original powder, within experimental error. However, PEEK powder I melt-annealed at 400 °C for 4 h showed an increase in reduced viscosity (to 1.3 dL/g) and ~2% of the sample could not be dissolved in sulfuric acid, which indicates that a cross-linking has occurred. Cross-linking probably begins in an early stage of a melt annealing and may deter crystallization.

The decrease in the onset and peak temperatures of powder I after the melt annealing above 400 °C (Figure 8) is not considered as a result of thermal reaction since powder II and the mixture (80% of powder I) do not show the same behavior. As shown in Table IV and Figure 4, the heats of crystallization do not change with melt-annealing temperature and time. This indicates minimal thermal reactions during the melt-annealings. Reactions such as decomposition, chain branching, and cross-linking may indeed occur in PEEK but too little an extent to influence the results.

Conclusions

Isothermal and nonisothermal crystallizations of PEEK with three different molecular weights have been characterized as a function of thermal history in the melt. As melt temperature was increased, isothermal crystallization exotherms shifted to longer time and crystallization curves on cooling shifted to lower temperatures. Crystallization on cooling for higher molecular weight sample was less sensitive to melt temperature. This has been explained by the existence of remnants of former crystals and small crystalline regions trapped in cavities of solid impurities. Both kinds of crystalline regions persist above the observed melting temperature and serve as nuclei for new crystallization.

As the holding time in the melt was increased, isothermal crystallization curves shifted to longer time. This is considered to be due to the high viscosity and chain entanglements in the melt. When PEEK was melted above 390 °C, the isothermal crystallization curves showed a rapid increase in peak crystallization time with melt-annealing time. When the melt temperature was 390 °C or above, the isothermal and nonisothermal crystallization behavior of PEEK have been found to be nearly independent of melt temperature. Since the thermodynamic melting point of PEEK (389, 395 °C) has been estimated to be in the vicinity of 390 °C, these different crystallization behaviors below and above 390 °C are considered to support the hypothesis that the remnants of former crystals persist up to the thermodynamic melting point. Several other semicrystalline polymers have also been found to support the hypothesis.

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Registry No. PEEK, 31694-16-3.

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