Double-Melting Behavior of Poly(ether ether ketone)

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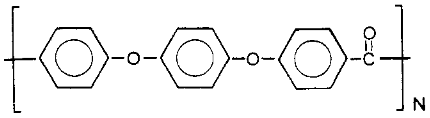
ABSTRACT: The melting behavior of semicrystalline poly(ether ether ketone) (PEEK) has been studied by differential scanning calorimetry (DSC). When PEEK is annealed or cold-crystallized from the amorphous glassy state at high supercooling or melt-crystallized at low supercooling, it usually shows two melting peaks. The low-temperature endotherm has been found to represent only a portion of the melting endotherm of original crystals. The high-temperature endotherm is the melting of crystals reorganized during a heating scan. This double-melting behavior can be explained by the sum of four contributions: melting of most original crystals, their recrystallization, remelting of recrystallized PEEK, and melting of residual crystalline regions. A Hoffman–Weeks plot using the high-temperature melting peak and the crystallization temperature (T_c) for the melt-crystallized PEEK ($T_c > 310$ °C) indicates that an equilibrium melting temperature is 389 ± 4 °C. As a result of isothermal crystallization and reorganization during a heating scan, the lamellae are found to be thickened by a factor of 1.7.

Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic with a crystallinity up to 48% and a glass transition at 143 °C. The chemical structure of PEEK is



Since PEEK shows good mechanical properties, it is currently being studied as a high-performance plastic and as a matrix for fiber-reinforced composites.[1,2] The observation of two distinct melting endotherms for PEEK during differential thermal analysis is of interest as a parallel to the double melting found for several other polymers. A variety of explanations has been offered.[3]

Different crystal structures have been found to cause the multimelting peaks for *trans*-1,4-polyisoprene,[4] isotactic polypropylene,[5] and poly(vinylidene fluoride).[6] Different morphological species of different lamellar thicknesses have been found for *cis*-1,4-polyisoprene.[7] Simultaneous melting and recrystallization has been verified as the origin of double melting of seveal polymers, including poly(ethylene terephthalate) (PET)[8-10] and isotactic polystyrene.[11,12] Sometimes more than one reason is responsible for multiple melting peaks.[4,13]

The double-melting behavior of PEEK has been mentioned and considered comparable to PET.[14] In the present report, detailed aspects and mechanisms of the double-melting behavior are discussed.

Experimental Section

PEEK powder was obtained from Imperial Chemical Industries (ICI), Wilton, U.K. The reported $\bar{M}_n$ and $\bar{M}_w$ are 14100 and 38600, respectively. Fully amorphous PEEK, in 0.3-mm-thick films, was made by compression molding at 400 °C for 10 min and then quenching into cold water. The densities of PEEK films were measured in a density column made from aqueous solutions of calcium nitrate at 23 °C.[15] Amorphous PEEK exhibits a density of 1.2631 ± 0.0005, in agreement with a reported value.[14]

Amorphous PEEK films were isothermally cold-crystallized either within the sample cell of a Perkin-Elmer DSC-2 or between preheated hot plates and quenched into cold water (cold-crystallized). A heating rate of 320 °C/min was used to avoid nonisothermal crystallization before thermal equilibration. Amorphous films were also annealed after nonisothermal crystallization (annealed). With a Perkin-Elmer DSC-4, the samples were heated to the annealing temperature at 80 °C/min. At this heating rate, a cold crystallization exotherm has a peak at 185 °C, and most of the crystallization is gone by 200 °C. Melt crystallization was conducted in a DSC-4 by rapid cooling (−200 °C/min) from the melt (400 °C for 10 min). After isothermal crystallization, the samples were cooled rapidly (−200 °C/min) to room temperature. To minimize complications arising from the low thermal conductivity of polymers,[16] the sample size for the PEEK film was restricted to 0.5–1.0 mg. Indium, tin, lead, and zinc were used for temperature calibrations at each heating rate. Isothermal crystallization and annealing temperatures were calibrated with extrapolated melting points of standards to zero heating rate. All crystallizations and heating scans were done under a nitrogen atmosphere. DSC traces were normalized to 1 mg of sample and shown in the figures.

Results and Discussion

Poly(ether ether ketone) (PEEK) can be quenched from the melt to produce an amorphous, glassy state at room temperature. PEEK can be crystallized either by cooling from the melt (melt-crystallized) or by heating from the amorphous state (cold-crystallized). When amorphous PEEK is heated at 20 °C/min in a differential scanning calorimeter (DSC), a cold-crystallization exotherm occurs about 30 °C higher than its glass transition temperature (143 °C). Cold- and melt-crystallization methods were used for PEEK crystallized at higher and lower degree of supercoolings, respectively. The DSC traces of PEEK show two melting endotherms after isothermal crystallization or annealing. Figure 1 shows DSC traces of annealed and melt-crystallized PEEK. As the annealing or crystallization time is increased, the low-temperature melting endotherm shifts to higher temperature; however, the high-temperature melting endotherm does not change. Isothermally cold-crystallized samples show the same behavior, and the peak temperatures are listed in Table I.

PEEK films, which had been isothermally crystallized at 220 °C for 75 h from the quenched glassy state, were scanned at different heating rates. The heats of fusion and peak temperatures of the low- and high-temperature melting endotherms are plotted vs. heating rate in Figures 2 and 3, respectively. As the heating rate was increased, the heat of fusion of the low-temperature endotherm increased but that of the high-temperature endotherm decreased. For the case of annealed PET or drawn nylon 6,6,[10,17] also two melting endotherms usually appear in the DSC heating scan and show behavior comparable to Figures 2 and 3. For those cases, it has been concluded that the low-temperature endotherm is the melting of crystals that exist prior to the heating scan and that the high-temperature endotherm is the result of melting of crystals formed by simultaneous melting and recrystallization (reorganization) during the DSC heating scan. As the heating rate was increased, the amount of crystalline region that has time to recrystallize decreased; this results in a smaller high-temperature melting endotherm and a larger

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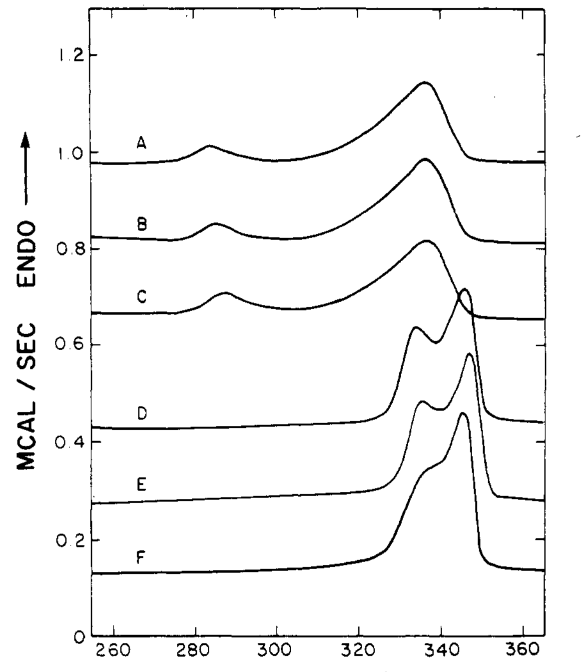

Figure 1. DSC traces for annealed and melt-crystallized PEEK (heating rate 20 °C/min): A, B, and C, annealed at 269.3 °C from the glassy state for 2, 4, and 10.2 h, respectively; D, E, and F, crystallized at 319.6 °C from the melt (400 °C, 10 min) for 14, 22.5, and 35 h, respectively.

Table I
Low- and High-Melting Peak Temperatures^a (T_m1 and T_m2, Respectively) and Densities for Isothermally Crystallized and Annealed PEEK

T_c or T_a, °C	time, h	T_m1, °C	T_m2, °C	density, g/cm^3
	Cold-Crystallized PEEK			
200.0	1.0	220.8	337.4	1.293
200.0	4.0	224.1	336.6	1.293
200.0	18.5	227.2	337.0	1.294
200.0	42.5	229.6	337.4	1.294
	Annealed PEEK			
200.0	1.0	219.2	337.7	1.2925
250.0	1.0	267.9	337.0	1.2974
269.3	1.0	284.2	336.6	1.2991
269.3	2.0	284.5	336.6	1.2993
269.3	4.0	286.0	336.7	1.2999
269.3	10.2	287.7	336.6	1.3004
290.0	1.0	303.3	336.5	1.3011
320.0	1.0	330.4	336.9	1.3045
320.0	21.5	b	b	1.3064
	Melt-Crystallized PEEK			
314.3	5.6	328.7	344.7	1.3063
316.0	14.5	331.3	345.8	1.3091
318.6	14.0	334.9	347.7	
319.6	14.0	334.8	347.6	1.3087
319.6	22.5	335.5	347.4	1.3092
319.6	35.0	338.8	347.4	1.3096
322.8	20.0	339.1	350.5	1.3060
323.6	25.0	339.8	349.6	1.3052
328.6	34.0	344.3	352.8	1.3069

[a] Measured by DSC at a heating rate 20 °C/min. [b] Shows only one peak at 335.8 °C.

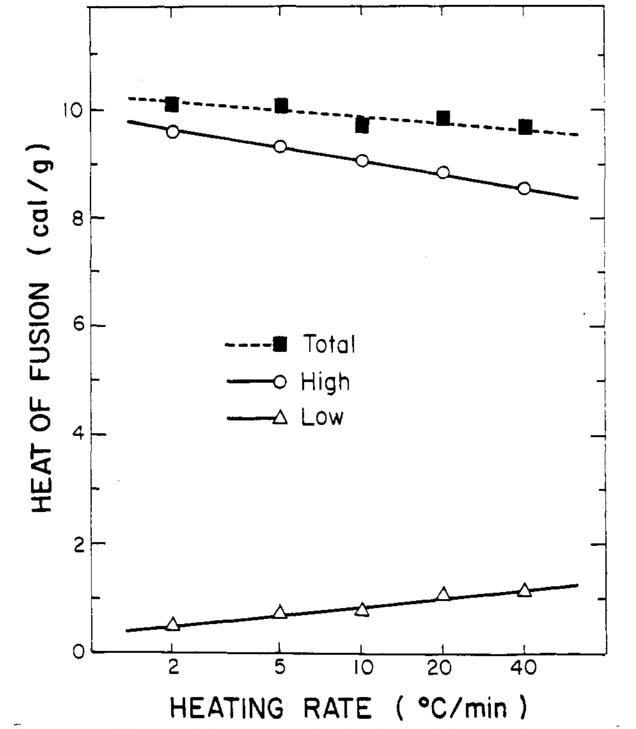

Figure 2. Heats of fusion of the high- and low-melting peaks vs. heating rate. The PEEK samples were cold-crystallized at 220 °C for 75 h.

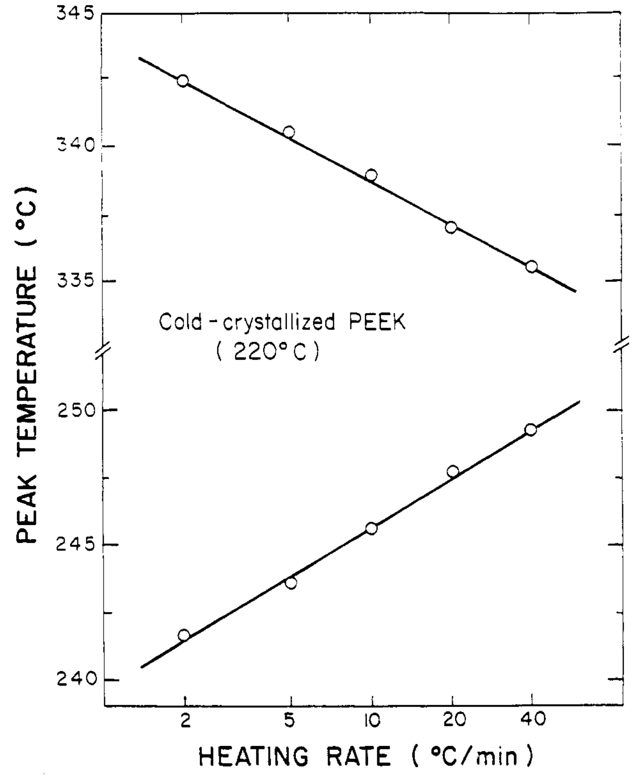

Figure 3. The two melting peak temperatures vs. heating rate. The PEEK samples were cold-crystallized at 220 °C for 75 h.

low-temperature melting endotherm in Figure 2. The total heat of fusion for both endotherms decreases slightly with increasing heating rate, due to restricted annealing on heating.

Figure 3 shows that the peak temperature of the high-temperature endotherm (T_m2) is decreased but the peak temperature of the low-temperature endotherm (T_m1) is increased, at increased heating rate. The decrease in T_m2 with heating rate may be explained in terms of the shorter reorganization times; the size and perfection of the recrystallized PEEK decreases with increasing heating rate. These results are consistent with studies on the several polymers showing double-melting peaks due to the reorganization process.[4,10,11,17] Recrystallization or reorganization of cold-crystallized PEEK has been found in an

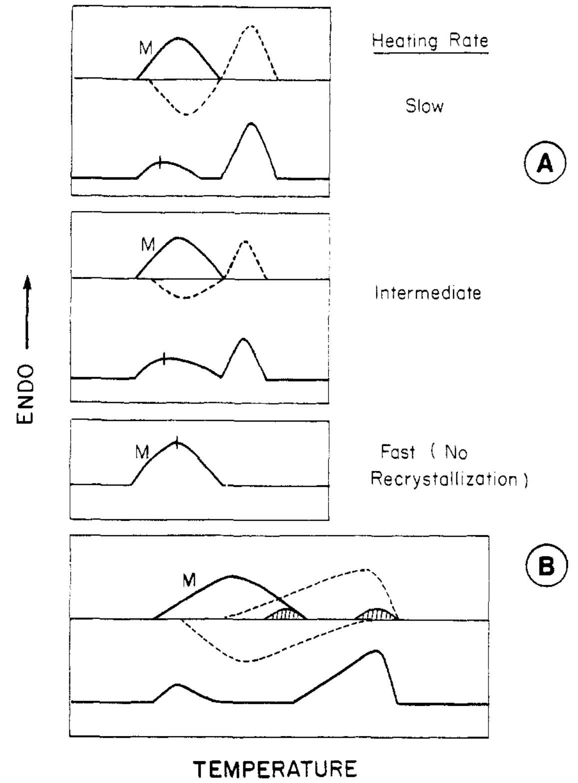

Figure 4. (A) Schematic representation of the melting mechanism proposed for poly(ϵ-caprolactone) (adapted from ref 20). (B) Proposed melting mechanism for PEEK. M represents the melting endotherm of the original crystals. The dotted lines represent the recrystallization exotherm and the melting endotherm of the recrystallized materials. The shaded area in B represents melting endotherms of the core crystalline region.

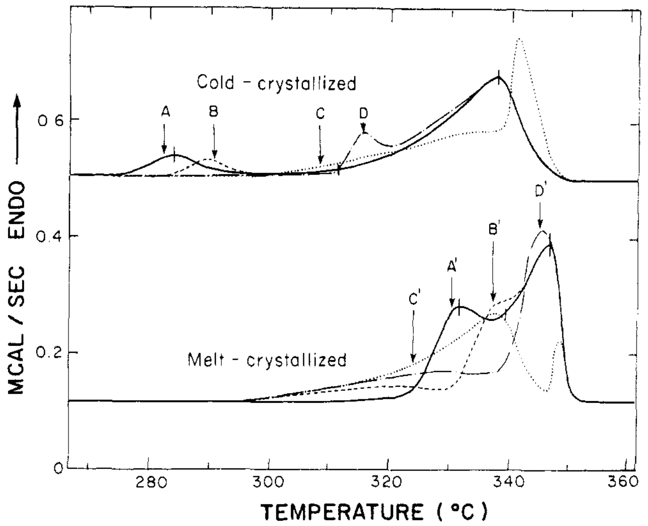

Figure 5. DSC traces (20 °C/min) of cold-crystallized PEEK at 270 °C for 2 h (A), and melt-crystallized PEEK at 316 °C for 14.5 h (A′). The heating scan was stopped at the low-temperature melting peak (T_m1) for B and B′; at the high-temperature melting peak (T_m2) for C and C′; and in the middle of T_m1 and T_m2 for D and D′. When the scan was stopped, each sample was immediately cooled and a second scan (20 °C/min) begun. The stopping temperatures (T_s) indicated on curve A′ are 332, 339, and 346 °C; on curve A they are 285, 312, and 338 °C.

analysis using solid and liquid heat capacity.[18] Examples for the superheating of macromolecules and their explanations have been reported.[3] The superheating of relatively large perfect macromolecular crystals that have the extended chain conformation has been explained to be due to the intrinsic slowness of crystal melting or due to an initial reduction of the entropy on melting. The small nonequilibrated crystals may superheat due to strained amorphous tie molecules or due to special molecular conformations at the crystal surface showing a reduced entropy of fusion on melting. From the following, we believe that the two melting endotherms of PEEK do not represent two morphologically different crystals or lamellar species; therefore, the superheating of the low-temperature melting peak should be explained in connection with the high-temperature melting peak. Wide-angle X-ray scattering (WAXS) experiments indicate only one crystal structure for both melt- and cold-crystallized PEEK. The reflection planes are in agreement with those reported for an orthorhombic unit cell.[19] No evidence for two lamellar structures for either melt- or cold-crystallized PEEK has been found with small-angle X-ray scattering (SAXS). Detailed WAXS and SAXS results will be reported elsewhere.

Rim and Runt have considered the double melting of poly(ϵ-caprolactone) as a combination of the three peaks due to the melting of original crystals, recrystallization, and melting of the recrystallized materials, as shown in Figure 4A.[20] The areas of the recrystallization exotherm and the melting endotherm of the recrystallized material are the same. At a low heating rate, there will be a large recrystallization exotherm under the melting endotherm of original crystals and another melting endotherm of the recrystallized material (remelting peak) at high temperature. As the heating rate is increased, the crystals will have less time to reorganize; thus the recrystallization exotherm, and consequently the remelting endotherm, will decrease in magnitude. At a high heating rate, however, recrystallization is restricted so that the melting of original crystals will be observed directly. When the heating rate is high, the effect of thermal conductivity will be considerable; therefore, superheating due to the low thermal conductivity of polymers will be observed.[3,20] The superheating of T_m1 in Figure 3 can be explained by the sums of the three peaks for different heating rates as shown in Figure 4A. It is important to note the little resemblance between the melting endotherm of the original crystals and the low-temperature endotherm. The low-temperature melting endotherm observed in a heating scan is determined by the sum of the recrystallization exotherm and the melting endotherm of original crystals.

The shape of the recrystallization exotherm cannot be measured directly by DSC, since only the net sum of two opposing contributions is detected. However, the following experiments can give an idea of the shape of the recrystallization exotherm. Heating scans were stopped at the peak temperatures of the low- and high-tempeature endotherms and in the middle of two melting peaks, whereafter the samples were immediately cooled (−150 °C/min) and rescanned. Figure 5 shows the first and three of the second scans for cold- and melt-crystallized PEEK. For all, the second scan shows a new melting endotherm at a temperature greater than the stopping temperature (T_s), due to the melting of material recrystallized up to T_s. A new, large endotherm above T_s in curve C indicates that the recrystallization still occurs at T_m2 for cold-crystallized PEEK. This suggests that the recrystallization exotherm and remelting endotherm of PEEK overlap (see Figure 4). The broad melting endotherm at a temperature below T_s is the evidence of the crystalline region that failed to recrystallize in the first scan and crystallized on cooling. As T_s is increased, a broader melting endotherm below T_s is observed. Curve C′ for melt-crystallized PEEK shows a large broad endotherm below T_s, indicating that most crystals have melted without recrystallization up to T_s.

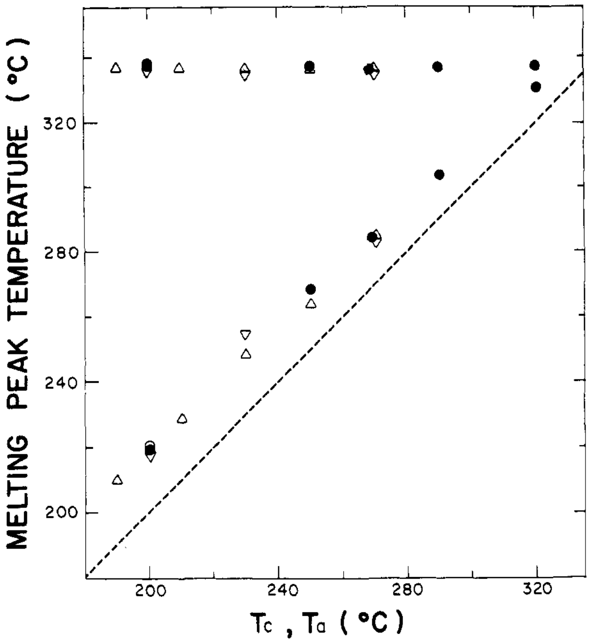

Figure 6. T_m1 and T_m2 of isothermally cold-crystallized (△, ▽, ○) and annealed (●) PEEK vs. crystallization (T_c) or annealing temperature (T_a). Crystallization or annealing time is 1 h and the DSC heating rate is 20 °C/min, except for (△). (△) Data of ref 18. Crystallization time is 2 h and DSC heating rate is 10 °C/min. (▽) Data of ref. 14. The dashed line is for $T_m = T_c$.

Less of the broad endotherms are observed below T_s than the amount of melting endotherm up to T_s in the first scan. This is more pronounced in the cold-crystallized PEEK than in the melt-crystallized sample. This result is in accord with the suggestion that the reorganization process involves more recrystallization for PEEK crystallized at higher supercooling.[18] If the low-temperature melting endotherm were due to the melting of another different crystalline species or the entire melting of the original crystals, the endotherms below T_s would be equal amount for both the first and second scan. This result supports that the low-temperature endotherm represents only a portion of the melting of the original crystals that exist in the sample prior to heating scan (see Figure 4). Therefore, using T_m1 as the melting peak temperature of the original crystals is considered to be groundless.[14,21] Moreover, as shown in Figure 3, the measured T_m1 varies by about 8 °C depending on the heating rate, which presents difficulties in determining the melting peak temperature of the original crystals for use in eq 1.

Figure 6 shows the two peak temperatures for isothermally crystallized and annealed PEEK from the amorphous state. The isothermal data of reference 14 and 18 are included. T_m1 and T_m2 of samples annealed after nonisothermal crystallization (peak at 185 °C) are very close to those of isothermally crystallized PEEK; T_m1 is located 10–20 °C higher than the crystallization temperature (T_c) or annealing temperature (T_a), and T_m2 is almost constant regardless of T_c or T_a. This may be due to imperfect, small crystals that are ready to melt and recrystallize since they were produced at low temperature (around 185 °C). It has been shown that such imperfect crystals melt just above their formation temperature and reorganize into more perfect crystals by successive heating scans.[22]

Table I shows the two melting temperatures and densities for isothermally crystallized and annealed PEEK. With increasing T_a, the sample density is increased more sensitively than with annealing time. In contrast to the annealed or cold-crystallized samples, the melt-crystallized PEEK shows an increase in T_m2 with increasing T_c. The samples cold-crystallized at 200 °C or melt-crystallized at 319.6 °C show that T_m2 is constant but T_m1 and density increase with increasing crystallization time. Samples annealed at 269.3 °C also show this same behavior. Since T_m1 increases more sensitively than density, some other reasons besides an increase in crystallinity is needed. For PET, it has been concluded that smoothing of the crystal folding surfaces occurs during isothermal crystallization, which results in an increase in T_m1.[8] According to the Thomson–Gibbs equation (eq 1), increased regularity in the chain conformation at the crystal surface reduces the surface energy (σ_e) and increases the melting temperature of original crystals. The high-temperature-shifted melting endotherm of original crystals is subtracted by the recrystallization exotherm to produce a high-temperature-shifted low-temperature endotherm (Figure 4A). Besides smoothing of the folding surfaces, regularization of lateral surfaces and rejection of defects have been suggested as responsible for the increase in T_m1 as the annealing time of PET is increased.[9]

As discussed previously, the high-temperature endotherm is the melting of recrystallized PEEK resulting from a reorganization. Crystal surfaces are metastable due to the existence of chain folds, loops, cilia, and tie molecules. Zachmann and Peterlin have suggested that melting or crystallization can occur at the crystal surface, even when the overall crystal is stable.[23] Arakawa et al. have shown that the reorganization is inhibited by chemical reaction on the crystal surfaces and in the amorphous region.[24] After methoxymethylation, the double-melting peaks of nylon 6 were changed to a single peak that did not depend on heating rate. The surface melting before core melting has been observed for polyethylene with SAXS.[25] Therefore, the reorganization process is considered as a partial melting followed by simultaneous recrystallization at the crystal surface. This reorganization process, occurring at the crystal surfaces, may prevent some core crystalline portions from melting. The model shown in Figure 4A has been modified to accommodate the above observations for PEEK. The major points of this model, shown in Figure 4B, are outlined as follows:

i. The magnitude of the recrystallization exotherm at a temperature depends on the amount of crystals that have melted and decreases with increasing temperature due to a lower degree of supercooling.

ii. Recrystallization ends below T_m2 in PEEK melt crystallized at low supercooling and above T_m2 in cold-crystallized samples.

iii. Recrystallized material melts at a temperature several degrees higher than its recrystallization temperature.

iv. Some core portion of the original crystals melts at the temperature where the reorganization process ends. This new model can explain the superheating of T_m1 similarly to the one in Figure 4A.

PEEK films melt crystallized at a lower degree of supercooling were scanned at different heating rates. The measured T_m1 and T_m2 are shown in Figure 7. In contrast to PEEK cold-crystallized at high supercooling, T_m2 does not change with heating rate (2–40 °C/min). The difference in the melting behavior of two PEEK samples may be related to the crystalline morphology that was produced at different degrees of supercooling. Also in comparison to melt-crystallized PEEK, cold-crystallized PEEK has been found to have spherulites smaller by an order of magnitude and thinner lamellae due to higher nucleation density.[26] Owing to slow crystallization, the chain con-

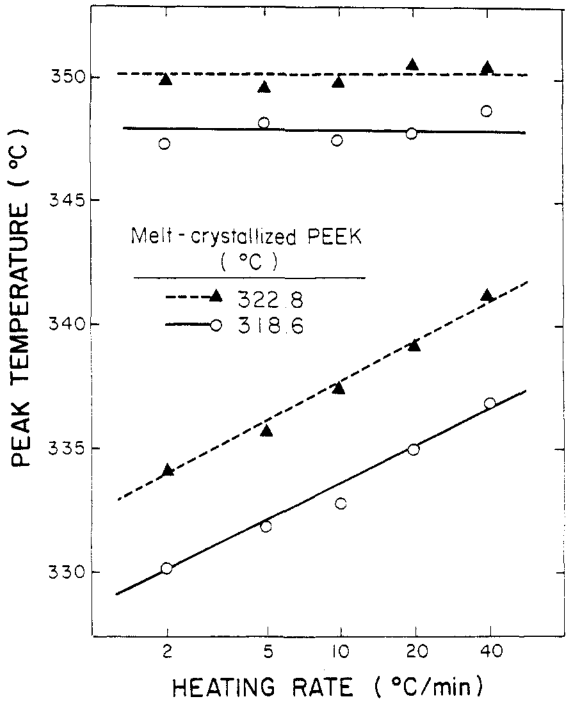

Figure 7. T_m1 and T_m2 of melt-crystallized PEEK at 322.8 °C for 20 h (▲) and at 318.6 °C for 14 h (○) vs. heating rate.

formations at the crystal surfaces are more perfect in the PEEK crystals that were melt-crystallized at low supercooling than those in cold-crystallized samples. The temperature range of reorganization for the melt-crystallized PEEK is small, as shown in Figure 1. Therefore, the reorganization process of a melt-crystallized PEEK occurs easily and within the heating rates. Also the same size and perfection of crystals is produced through the fast reorganization process regardless of heating rate. DSC traces for melt-crystallized PEEK may be represented by more overlap of the four peaks in Figure 4B. The area ratio of the low- and high-temperature endotherms in Figure 1 suggests that a smaller recrystallization exotherm is involved in the heating scan of a melt-crystallized PEEK than in that of an annealed PEEK. Curve C′ of melt-crystallized PEEK in Figure 5 shows a new melting endotherm above T_s with the same magnitude as that in the first scan. This indicates that the recrystallization of melt-crystallized PEEK ends below T_m2. Superheating of T_m1 is also observed and can be explained in the same way as that in cold-crystallized PEEK.

In Figure 8 are plotted T_m1 and T_m2 schematically with T_c for melt- and cold-crystallized PEEK. T_m1 from both crystallization methods exhibits a range essentially parallel to the $T_m = T_c$ line. Recall that T_m1 increases as the crystallization time increases (Figure 1 and Table I). T_m2 of cold-crystallized PEEK shows an almost constant temperature (~337 °C) regardless of crystallization temperature and time. In contrast, T_m2 of melt-crystallized PEEK ($T_c > 310$ °C) falls on a line with a slope of 0.60.

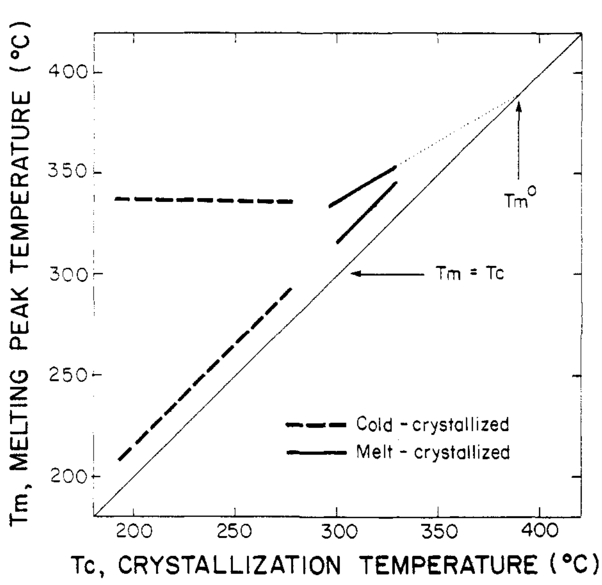

Figure 8. Two melting peak temperatures vs. crystallization temperatures for cold- and melt-crystallized PEEK.

In the case of laterally large lamellae, only the top and bottom surfaces contribute significantly to the free enthalpy of the crystal, so that the Thomson–Gibbs equation can be simplified to[3]

$$T_m = T_m^0[1 - 2\sigma_e/(\Delta h_f l)] \quad (1)$$

where T_m^0 is the equilibrium melting temperature, σ_e the top and bottom surface free energy, Δh_f the heat of fusion, and l the lamellar thickness. When it is assumed that the lamellar thickness achieves a final value on the average at the end of a crystallization experiment or a lamellar thickening process, the final lamellar thickness (l) will be γ times larger than the initial thickness (l_g^*).

$$l = \gamma l_g^* \quad (2)$$

According to the kinetic theory of Lauritzen and Hoffman,[27,28] the initial thickness (l_g^*) of a chain-folded lamella, which is kinetically determined, is expressed by

$$l_g^* = (2\sigma_e/\Delta f) + \delta l = [2\sigma_e T_m^0/(\Delta h_f \Delta T)] + \delta l \quad (3)$$

where Δf is the free enthalpy per unit volume of crystal, ΔT the supercooling ($T_m^0 - T_c$) and δl a small positive quantity that is only a weak function of the supercooling. Since $2\sigma_e/\Delta f \gg \delta l$ is a fair approximation for the crystal formed at low supercooling, the following equation is derived by inserting eq 2 and 3 into eq 1:

$$T_m = T_m^0(1 - 1/\gamma) + (1/\gamma)T_c \quad (4)$$

Equation 4 shows that T_m^0 and the lamellar thickening factor (γ) are determined from the intersection with the $T_m = T_c$ line and the slope, respectively, in a Hoffman–Weeks plot of T_m vs. T_c.[29] Since recrystallization can more rapidly produce crystalline material than ordinary isothermal crystallization at the same temperature, concerns about the effects of recrystallization on the observed melting temperature have been discussed.[29,30] When T_m2 is considered to be the melting temperature in eq 4, the T_m^0 of PEEK is measured to be 389 ± 4 °C, about 6 °C lower than the previously reported value.[14] As discussed, the reorganization process involves partial melting and recrystallization at the crystal surfaces, and the reorganized crystals may be larger than the original crystals. T_m2 of melt-crystallized PEEK at a low supercooling ($T_c > 310$ °C) shows a linear relationship with T_c but no dependence on the crystallization time and heating rate. These results suggest that the reorganization process increases the crystal dimensions rapidly up to a limit determined only by T_c. Therefore, T_m2, the melting peak temperature of reorganized crystals, may be treated as the melting temperature of thickened crystals at the end of a crystallization.

T_m1 and T_m2 of the melt-crystallized PEEK are shown in Figure 9. The crystallization times are listed in Table I or are similar to the listed values. Recall that T_m2 is not sensitive to crystallization time. From the slope of the line in Figure 9, γ is calculated to be 1.7. During the crystallization the initial PEEK lamellae may be thickened,

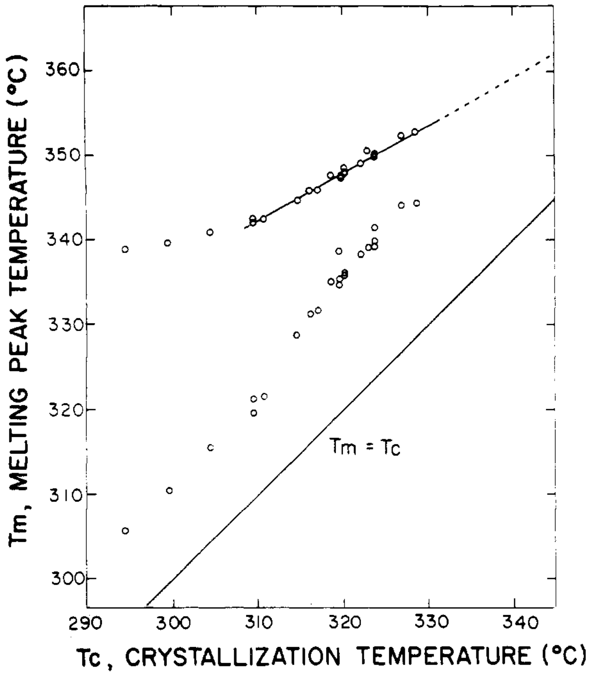

Figure 9. Two melting peak temperatures (at 20 °C/min) of melt-crystallized PEEK vs. crystallization temperatures.

and these lamellae are further increased in size during the heating scan in DSC. The final PEEK lamellar thickness, after reorganization, reaches 1.7 times the initial thickness. Lamellar thickening factors during isothermal crystallization have been found to be 2–2.5 for polyethylene,[28,31] 2 for isotactic polystyrene,[12] and 3.4 for poly(chlorotrifluoroethylene).[27,29] The T_m2 of melt-crystallized PEEK below 310 °C does not show a linear relationship with T_c and approaches T_m2 of cold-crystallized PEEK as T_c is decreased.

Conclusions

The double-melting behavior of PEEK has been found to be due to a crystal reorganization on heating. The low-temperature endotherm has been found to represent only a portion of the melting endotherm of original crystals. The high-temperature endotherm is the melting of crystals reorganized during a heating scan. The reorganization process is considered to occur at crystal surfaces through a partial melting followed by recrystallization. The model modified from the one proposed by Rim and Runt is consistent with the melting behavior of PEEK. The low- and high-temperature melting peaks are considered to be the sum of four peaks: melting of most original crystals, their recrystallization, remelting of recrystallized material, and melting of core crystalline regions.

For melt-crystallized PEEK at lower supercooling (T_c > 310 °C), it is proposed that the reorganization process increases the crystal dimensions rapidly up to a limit determined by supercooling. A Hoffman–Weeks plot shows that the equilibrium melting temperature of PEEK is 389 ± 4 °C and the lamellar thickening factor is 1.7. During the isothermal crystallization, the initial lamellae may be thickened, and these lamellae are further increased in size during the heating scan. The final lamellar thickness after reorganization reaches 1.7 times the initial lamellar thickness.

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Registry No. PEEK, 31694-16-3.

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