SBR with phenylacetylphenyl groups compared with the corresponding SBR/deoxybenzoin mixture. The covalent bonding of the photosensitive group to polymer chain has a marked influence on the results. The explanation could lie in the well-known fact that the magnetic field effect depends strongly on the lifetime of the radical pairs.[5] It is obvious that segments of macromolecules in a solvent-free polymer matrix do not always have the same mobility as low molecular molecules in this matrix. Thus, the lifetime should be different for a radical pair consisting of a low molecular and a macroradical compared with a radical pair consisting of two low molecular radicals.

Registry No. $C_6H_5CH_2COC_6H_5$, 451-40-1; $C_6H_5COC_6H_5$, 119-61-9; $C_6H_5CH_2COCH_2C_6H_5$, 102-04-5; $C_6H_5COC_6H_4CH_3$, 134-84-9.

References and Notes

(1) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; Wiley: Chichester, 1987.
(2) Horie, K.; Ando, H.; Mita, I. *Macromolecules* **1987**, *20*, 54.
(3) Ng, H. C.; Guillet, J. E. *Macromolecules* **1985**, *18*, 2294.
(4) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985.
(5) Reviews: Atkins, P. W.; Lambert, T. P. *Annu. Rep. Chem. Soc., Sect. A: Phys. Inorg.* **1975**, *67*. Salikhov, K. M. In *Spin Polarization and Magnetic Effects in Radical Reactions*; Molin, Yu. N., Ed.; Elsevier: Amsterdam, 1984; Chapter 3. Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609.
(6) Turro, N. J.; Mattay, J. *J. Am. Chem. Soc.* **1981**, *103*, 4200, and subsequent papers.
(7) Tanimoto, Y.; Shimizu, K.; Itoh, M. *J. Am. Chem. Soc.* **1984**, *106*, 7257.
(8) Martl, M. G. Thesis, Technische Universität Graz, 1984.
(9) Morita, H.; Higasayama, I.; Yamaoka, T. *Chem. Lett.* **1986**, 963.
(10) Schaller, R.; Martl, M. G.; Hummel, K. *Eur. Polym. J.* **1987**, *23*, 259.
(11) Hummel, K.; Schaller, R.; Martl, M. G. *Polym. Bull. (Berlin)* **1987**, *17*, 369.
(12) Martl., M. G.; Pongratz, Th.; Hummel, K. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 649.
(13) Martl, M. G.; Schaller, R.; Hummel, K. *Makromol. Chem.* **1985**, *186*, 2615.
(14) Leshina, T. V.; Salikhov, K. M.; Sagdeev, R. Z.; Belyaeva, S. G.; Mariasova, V. I.; Purtov, P. A.; Molin, Yu. N. *Chem. Phys. Lett.* **1980**, *70*, 228.
(15) Turro, N. J.; Chung, C.-J.; Jones, G.; Becker, W. G. *J. Phys. Chem.* **1982**, *86*, 3677.
(16) Kreyszig, E. *Statistische Methoden und ihre Anwendungen*, 7th ed.; Vandenhoeck & Ruprecht: Göttingen, 1979; p 218.
(17) Schaller, R. Thesis, Technische Universität Graz, 1987.
(18) Heine, H. G. *Tetrahedron Lett.* **1972**, *33*, 3411.
(19) Ng, H. C.; Guillet, J. E. *Macromolecules* **1985**, *18*, 2299.
(20) Scaiano, J. C.; Abuin, E. B.; Steward, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.
(21) Sakaguchi, Y.; Nagakura, S.; Hayashi, H. *Chem. Phys. Lett.* **1980**, *72*, 420.
(22) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.
(23) Berndt, A.; Fischer, H.; Paul, H. *Magnetic Properties of Free Radicals*; Landolt-Börnstein; Springer-Verlag: Berlin, 1977; Group II, Vol. 9, Part b.

On the Double-Melting Behavior of Poly(ether ether ketone)

Youngchul Lee,*,† Roger S. Porter,† and J. S. Lin‡

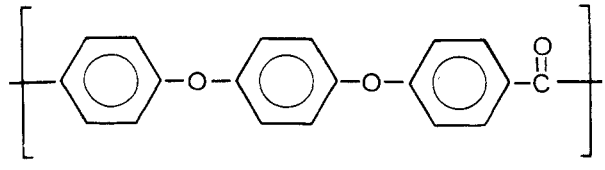
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, and Solid State Division, Oak Ridge National Laboratory,§ Oak Ridge, Tennessee 37831.

Received June 14, 1988; Revised Manuscript Received September 12, 1988

ABSTRACT: The double-melting behavior of poly(ether ether ketone) (PEEK) has been investigated using differential scanning calorimetry (DSC) and wide- and small-angle X-ray scattering. The peak temperatures of two melting endotherms have been found to depend linearly on the logarithm of the DSC heating rate. At a high heating rate, two endotherms coalesce into a single endotherm which has been considered to represent complete melting without reorganization. The peak temperature of the coalesced endotherm has been found to be approximately the average of the two former peak temperatures at lower heating rates. This behavior has also been observed for poly(ethylene terephthalate) which is known to show two melting endotherms due to crystal reorganization. The average of the two peak temperatures, therefore, has been used in the Thomson–Gibbs equation to estimate the thermodynamic melting point (384 °C) and surface free energy (39 erg/cm^2) of the PEEK crystal. The heat of fusion of the PEEK crystal (39.5 cal/g) has been measured from a linear relationship between the heat of fusion and the density.

Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic with a glass transition around 145 °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.[1-7]

Differential scanning calorimeter (DSC) traces of PEEK samples which have been isothermally crystallized show two distinct melting endotherms.[8-11] The observation of

* Current address: Textile Processing Laboratory, University of Tennessee, Knoxville, TN 37996.
† University of Massachusetts.
‡ Oak Ridge National Laboratory.

§ Operated by Martin Marietta Energy Systems, Inc., for the Division of Materials Sciences, US Department of Energy under Contract DE-AC05-84OR21400.

0024-9297/89/2222-1756$01.50/0

Table I
Crystallization Temperature (T_c), Peak Temperatures of the Low- and High-Temperature Endotherms (T_m1 and T_m2), Average Melting Temperature ($\bar{T}_m$ Density (ρ), Crystallinity from Density (χ_ρ), Long Period (l), and Crystal Thickness (l_c) for Isothermally Crystallized and Annealed PEEK Films (0.3 mm Thick)[a]

T_c, °C	T_m1, °C	T_m2, °C	$\bar{T}_m$,[b] °C	ρ, g/cm^3	χ_ρ,[c] %	l, Å	l_c, Å
			Cold-Crystallized PEEK				
180	195.1	337.9	266.5	1.2898	17.6	101	17.8
190	207.8	337.7	272.8	1.2905	18.1	104	18.8
200	220.8	337.4	279.1	1.2929	19.7	104	20.5
200[d]	220.2	337.9	279.0	1.2926	19.5	104	20.3
210	230.2	336.8	283.5	1.2923	19.3	106	20.5
			Annealed PEEK				
200	219.2	337.7	278.5	1.2925	19.4	106	20.6
215	235.2	334.7	285.0	1.2936	20.1	115	23.1
230	251.5	335.3	293.4	1.2952	21.2	115	24.4
250	267.9	337.0	302.5	1.2974	22.6	119	26.9
269	284.2	336.6	310.4	1.2991	23.8	130	30.9
290	303.3	336.5	319.9	1.3011	25.1	137	34.4
310	323.6	337.7	330.7	1.3042	27.1	148	40.1
320	330.4	336.9	333.7	1.3045	27.3	157	42.9
320[e]	335.8	335.8	335.8	1.3064	28.6	157	44.9

[a] Crystallization time was 1 h except for the last listed. [b] $\bar{T}_m = (T_m1 + T_m2)/2$. [c] Using 1.415 and 1.263 g/cm^3 as crystal and amorphous densities, respectively. [d] Sample thickness was 0.1 mm. [e] Annealing time was 21.5 h.

two melting endotherms is of great interest as an analogy to the multimelting endotherms found for several other polymers.[12] The verified reasons are different crystal structures for *trans*-1,4-polyisoprene,[13] isotactic polypropylene,[14] and poly(vinylidene fluoride);[15] two crystalline populations with different size and/or perfection for a copolyether–ester[16] and *cis*-1,4-polyisoprene;[17] and crystal reorganization for poly(ethylene terephthalate),[18-21] isotactic polystyrene,[22,23] polyethylene,[24,25] and poly(oxymethylene).[26]

Double-melting behavior of PEEK has been previously found to be associated with crystal reorganization during heating.[8-11] The high-temperature endotherm is melting of the crystals which have been continuously reorganized from the original state during the heating. Previously, we proposed for PEEK that the low- and high-temperature endotherms resulted from the sum of four different contributions: partial melting of the original crystals, their recrystallization, melting of recrystallized crystals, and melting of core crystals.[8] Therefore, the low-temperature endotherm does not represent the complete melting of the original crystals. Also, the peak temperature of the low-temperature melting endotherm (T_m1) was found to depend strongly on heating rate.[8]

Blundell and Osborn believed that T_m1 of PEEK represented the melting point of the original crystals which existed in the sample prior to heating.[9] Therefore, they used T_m1 in the calculation of the thermodynamic melting point and surface free energy of the PEEK crystal. This point of view is to be critically discussed, and the true melting point of the original PEEK crystals prior to heating will be estimated.

Experimental Section

PEEK powder was obtained from Imperial Chemical Industries (ICI), Wilton, U.K. The reported $\bar{M}_n$ and $\bar{M}_w$ are 14 100 and 38 600, respectively. Fully amorphous PEEK, in 0.1- and 0.3-mm-thick films, was made by compression molding at 400 °C for 10 min and then quenching in cold water. The densities of the PEEK films crystallized at several isothermal temperatures were measured at 23 °C in a density gradient column made from aqueous solutions of calcium nitrate.[27] The sensitivity of the column was about 0.0001 g/(cm^3 mm); thus, the accuracy of the density measurement was 0.05% or better. The amorphous PEEK films used in this study exhibited a density of 1.2631 ± 0.0005, in agreement with a reported value.[9]

Amorphous PEEK films were isothermally cold crystallized by heating from room temperature in the sample cell of a Perkin-Elmer differential scanning calorimeter, DSC-2 (cold-crystallized samples). Although the fastest heating rate (320 °C/min) of the DSC was used, a temperature of 210 °C was the highest isothermal crystallization temperature attained without any crystallization before thermal equilibration. The amorphous films were also annealed by using a Perkin-Elmer DSC-4 (annealed samples). On heating to an annealing temperature at 80 °C/min, there occurs nonisothermal crystallization around 185 °C. Crystallization from the melt state (400 °C for 10 min) was also conducted in the DSC-4 by rapid cooling (−200 °C/min). After isothermal crystallization, the samples were cooled rapidly (−200 °C/min) to room temperature.

Amorphous poly(ethylene terephthalate) (PET) films (intrinsic viscosity, 0.83 dL/g) were annealed in an oven, under nitrogen atmosphere at 190 °C for 2 and 20 h. Annealed PET samples were scanned at various heating rates ranging 5–200 °C/min.

Indium, tin, lead, and zinc were used as standards for DSC calibrations of temperature and heat of transition at each heating rate. Isothermal crystallization and annealing temperatures were calibrated with extrapolated melting points of the standards to zero heating rate.[5] All the experiments with DSC were performed under dry nitrogen atmosphere. Samples of 0.1–5 mg were used after ensuring against saturation or broadness of heat flow due to large sample size.[28] DSC traces were normalized to 1.0 mg of sample, as shown in all the figures.

After crystallization, wide-angle X-ray diffraction patterns of the PEEK samples were examined by using a Siemens D-500 diffractometer equipped with a pulse-height scintillation counter. X-ray diffraction experiments were conducted in transmission mode with Ni-filtered Cu Kα radiation at 30 mA and 40 kV.

The long periods of morphological microstructures in PEEK samples were measured with the small-angle X-ray scattering (SAXS) facility at the National Center for Small Angle Scattering Research (NCSASR) at Oak Ridge National Laboratory, Oak Ridge, TN. The apparatus consists mainly of a pinhole-collimated Cu Kα X-ray source at 80 mA and 40 kV and a two-dimensional position-sensitive detector. Intensity was corrected for detector sensitivity, sample absorption, background, and dark current. The intensity was also Lorentz-corrected[29,30] to measure the long period from the angular position of intensity peak, using the Bragg equation.

Results and Discussion

PEEK films were crystallized either by cooling from the melt or by heating from the quenched amorphous state. Densities and heats of fusion plotted in Figure 1 were measured using a density gradient column and a differential scanning calorimeter (DSC), respectively. The net peak area method was used to measure heats of fusion.[31] Heats of fusion show a linear relationship with densities.

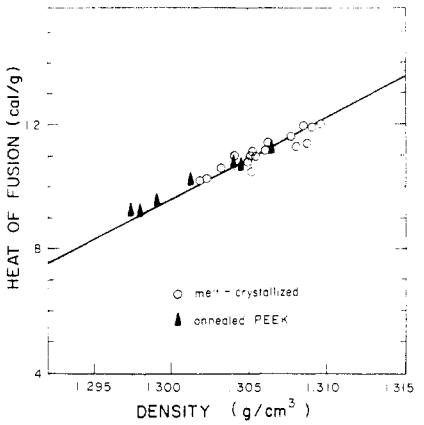


Figure 1. Heat of fusion for melt-crystallized and annealed PEEK. DSC heating rate was 20 °C/min.

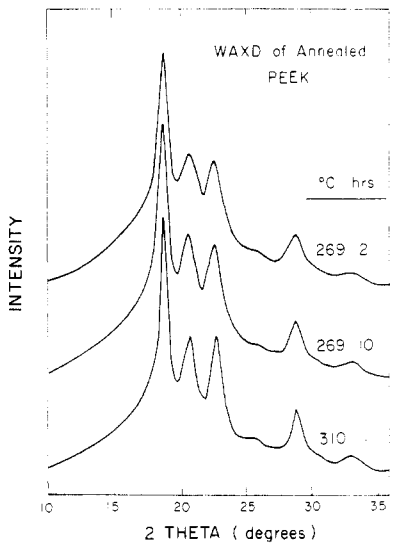


Figure 2. Wide-angle X-ray diffraction patterns of annealed PEEK. Annealing conditions are shown in the figure.

The crystallization conditions of PEEK are listed either in Table I or in our previous report.[8] A reproducible heat of fusion was not readily measured for PEEK crystallized at high supercooling, due to the curvature in DSC base line. A range of the PEEK crystal densities, calculated from the unit cell dimensions measured with wide-angle X-ray diffraction (WAXD), has been reported.[32-38] The X-ray diffraction patterns of PEEK drawn in our laboratory[5,7] and electron diffraction analysis of solution-grown PEEK crystals[39,40] are consistent with the unit cell dimensions reported by Rueda et al.[34] Therefore, their crystal density (1.415 g/cm^3) was used to calculate the heat of fusion for fully crystalline PEEK. The data points in Figure 1 extrapolate to 39.5 cal/g for fully crystalline PEEK at its melting point. Blundell and Osborn have measured the heat of fusion to be 31.1 cal/g using 1.401 g/cm^3 for the density of the PEEK crystal.[9]

Figure 2 shows wide-angle X-ray diffraction (WAXD) patterns of annealed PEEK. As annealing time or temperature was increased, diffraction peaks became sharper, indicating improvement of crystalline order. For poly(ethylene terephthalate) (PET), the same trends in WAXD patterns have been found and ascribed to an increase in the size of the mosaic blocks building up the lamellae.[41,42] WAXD patterns of PEEK samples, which show one and two melting endotherms in DSC traces, are the same in terms of diffraction peaks. This indicates that only one crystal structure exists in PEEK samples regardless of their melting behavior. It has been found that PEEK molecular chains pack in the crystal more densely with increased annealing temperature.[36]

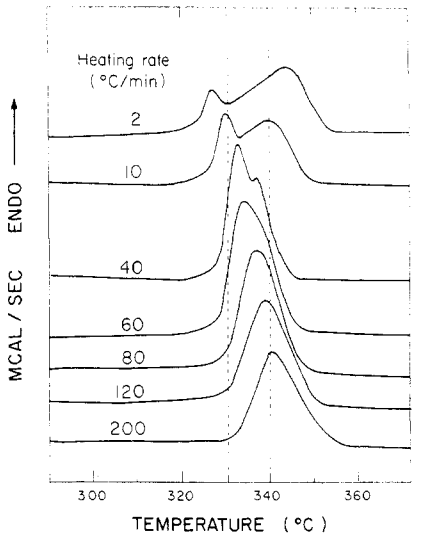


Figure 3. DSC traces of PEEK annealed at 320 °C for 1 h at various heating rates. Two dashed lines at 330 and 340 °C are for easier comparison.

In our previous report, the peak temperatures (T_m1, T_m2) and sizes of the two melting endotherms were found to depend on DSC heating rates.[8] This behavior was explained by simultaneous melting and recrystallization, i.e., crystal reorganization, during the DSC heating scan. Figure 3 shows DSC traces at various heating rates for PEEK annealed at 320 °C. As the heating rate was increased, the low-temperature melting endotherm increased in size and peak temperature, while the high-temperature endotherm decreased in size and peak temperature. The same behavior was reported previously for PEEK isothermally crystallized at 220 °C.[8] As the heating rate was increased, the amount of the crystalline regions which had time to recrystallize decreased; this resulted in a smaller high-temperature melting endotherm and a larger low-temperature melting endotherm. It was suggested that recrystallization is restricted at a high heating rate, so that the true melting of the original crystal might be observed without reorganization.[8,43] In Figure 3, the two distinct melting endotherms appear to coalesce into a single peak at ≥60 °C/min. It is noteworthy that the coalesced endotherm is located in the middle of the two former endotherms. For this particular sample, 60 °C/min appears to be fast enough to minimize the reorganization. The peak temperature of the merged single endotherm increases with increased heating rate above 60 °C/min. This may be due to the low thermal conductivity of a polymer; a similar behavior was reported for poly(ϵ-caprolactone).[44]

The peak temperatures of the PEEK sample in Figure 3 and another PEEK sample annealed at 310 °C are plotted versus heating rate in Figure 4. The two peak temperatures, T_m1 and T_m2, show a linear relationship with log (heating rate). The signs of the slopes of the two lines are opposite, and their absolute values are similar. The two peak temperatures of these annealed PEEK samples are lower than those of melt-crystallized PEEK, respectively, and the dependencies of T_m2 on heating rate for annealed and melt-crystallized PEEK are different due to different degrees of crystal perfection.[8]

The true melting point of the original crystals which exist prior to heating is difficult to measure due to annealing on heating. At a faster rate, observed melting peak is closer to the true melting point since annealing or reorganization is limited. However, superheating due to the

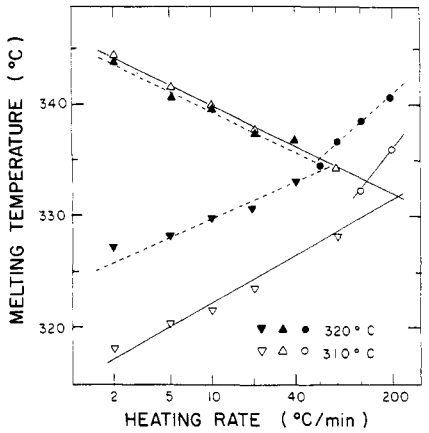


Figure 4. T_m1 and T_m2 of PEEK annealed at 310 °C for 1 h and at 320 °C for 1 h versus heating rate.

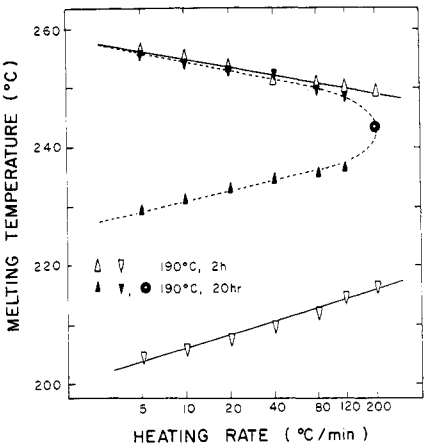


Figure 5. Two melting peak temperatures of poly(ethylene terephthalate) samples cold-crystallized at 190 °C for 2 and 20 h versus heating rate.

low heat conduction of a polymer arises at a fast heating rate. The single melting endotherm, without being superheated, in Figure 3 is considered to represent the true melting of the original PEEK crystals which existed in the sample prior to heating. Therefore, the true melting points of PEEK crystals annealed at 320 and 310 °C are considered to be 334.4 and 332.1 °C, respectively (Figure 4). It is interesting to note that these two true melting points are almost the same (within 2 deg for the two samples in Figure 4) as the arithmetic average of T_m1 and T_m2 at any low heating rates.

Isothermally crystallized or annealed poly(ethylene terephthalate) (PET) has also been known to show two melting endotherms in DSC due to crystal reorganization.[18-21] PET samples annealed at 190 °C for 2 and 20 h were scanned at various heating rates, and the two peak temperatures were plotted versus heating rate in Figure 5. The two peak temperatures show the same behavior as those of PEEK in Figure 4: T_m1 increases with increased heating rate, while T_m2 decreases with increased heating rate. This behavior of the two melting peak temperatures of PET has been previously observed;[18,19] however, coalescing of the two peaks at a fast heating rate has not been reported. At a scanning rate of 200 °C/min, the two melting endotherms coalesce into one endotherm with a peak temperature nearly in the middle of T_m1 and T_m2.

Arakawa et al. have shown that the crystal reorganization of nylon 6 is inhibited by a chemical reaction on the crystal surfaces and in the amorphous regions.[45] As the degree of methoxymethylation was increased, the two melting endotherms of nylon 6 shifted closer to each other.

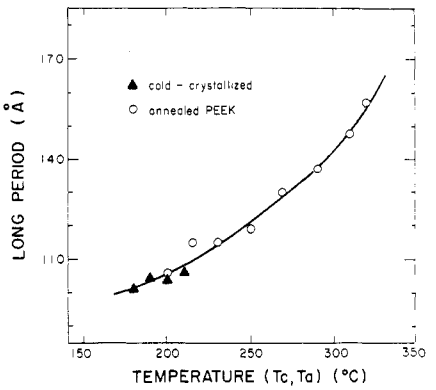


Figure 6. Long period versus crystallization temperature for cold-crystallized and annealed PEEK.

They finally coalesced into a single peak between the two former peaks. This reinforces the hypothesis that the true melting can be obscured by continuous melting and recrystallization when reorganization is allowed.

Blundell and Osborn measured the thermodynamic melting point ($T_m°$) of PEEK to be 395 °C[9] by using the Thomson–Gibbs equation[12]

$$T_m = T_m°\{1 - 2\sigma_e/(\Delta h_f \rho_c l_c)\} \quad (1)$$

where $T_m°$ is the thermodynamic melting point, σ_e the specific surface free energy of the top and bottom of lamellae, Δh_f the heat of fusion, ρ_c the density of the crystal, and l_c the crystal thickness. They used the peak temperature of the low-temperature endotherm (T_m1) as T_m in the eq 1. However, as discussed previously, the low-temperature endotherm is only a portion of melting of the original crystals, and the rest of the melting endotherm is not observed due to compensation by the recrystallization exotherm. It was shown that only about 10% of the original crystals melt without reorganization at the low-temperature endotherm for PEEK crystallized at high supercoolings.[8] Therefore, T_m1 is considered not to represent the true melting point of the original crystals prior to heating. Moreover, T_m1 strongly depends on heating rate as shown in Figures 3 and 4; T_m1 increases by 6 deg when the heating rate was increased from 2 to 40 °C/min.

The long periods of cold-crystallized and annealed PEEK from the glassy state were measured by using small-angle X-ray scattering.[29,30] One-dimensional crystalline and amorphous layers have been assumed; thus, the long period consists of one crystalline and one amorphous layer. The long period increased with increased annealing temperature, as shown in Figure 6. Little difference was observed between annealed and cold-crystallized PEEK. The crystal thickness (l_c) was calculated using the long period and crystallinity from density of the sample. The long period, crystallinity, and crystal thickness are listed in Table I. Also T_m1 and T_m2, observed at 20 °C/min, and $\bar{T}_m$ or $(T_m1 + T_m2)/2$ are added.

Since $\bar{T}_m$ is considered to be close to the true melting point of the original crystals, $\bar{T}_m$ is plotted versus $1/l_c$ in Figure 7. The data show a linear relationship which yields a thermodynamic melting point, $T_m°$ of 384 °C and surface free energy, σ_e, of 39 erg/cm^2 for the PEEK crystal. A comparable value of $T_m°$ (389 °C) was previously obtained by us using a Hoffman–Weeks plot.[8] Three data from ref 9 were included in Figure 7 after being treated as our data. They show appreciable consistency with our data. Although it is not considered to be adequate to use T_m1 as the true melting point of the original crystals, T_m1 is also plotted versus $1/l_c$ in Figure 7. The linear relationship of T_m1 with $1/l_c$ yields a $T_m°$ of 420 °C and σ_e of 67 erg/cm^2,

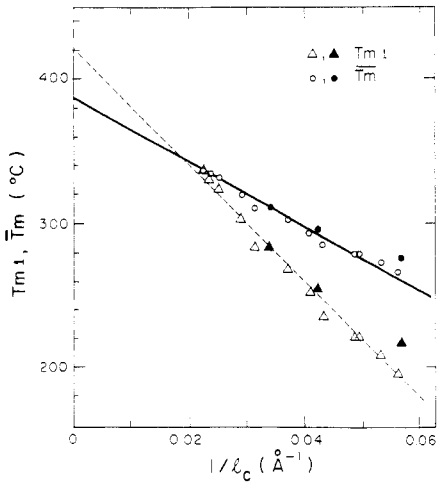


Figure 7. T_m1 and $\bar{T}_m$ versus 1/(crystal thickness). Solid symbols (▲, ●) are from ref 9.

which may vary with the scanning rate of DSC, since T_m1 depends on heating rate, as shown in Figure 4. These values of $T_m°$ and σ_e are considerably different from the values (395 °C and 49 erg/cm^2) previously reported in ref 9.

Conclusions

The double-melting behavior of PEEK as a function of heating rate of differential scanning calorimetry (DSC) has been detailed. The peak temperatures of the two melting endotherms have been found to depend linearly on logarithm of the DSC heating rate. The two melting endotherms of PEEK coalesce into one at high heating rates. The peak temperature of the coalesced endotherm is approximately in the middle of the two former peak temperatures. The same behavior has been found for poly(ethylene terephthalate), also known to show two melting peaks due to crystal reorganization. The coalesced endotherm is considered to represent the complete melting of the original crystal without reorganization.

By use of the average of two peak temperatures and the crystal thickness measured by small-angle X-ray scattering, the thermodynamic melting point and surface free energy of the PEEK crystal have been determined to be 384 °C and 39 erg/cm^2, respectively.

Wide-angle X-ray diffraction patterns of PEEK samples have shown that only one crystal structure exists regardless of multiplicity of melting endotherms and that crystalline order improves with increased annealing time or temperature. The heat of fusion for fully crystalline PEEK has been measured to be 39.5 cal/g at its melting point, using a linear relationship between the heat of fusion and the density.

Acknowledgment. We express our appreciation to the Office of Naval Research for the support of this study. We are grateful to Jia Guan for providing amorphous poly(ethylene terephthalate) films.

Registry No. PEEK, 31694-16-3.

References and Notes

(1) Rigby, R. B. *Polym. News* **1984**, *9*, 325.
(2) Nguyen, H. X.; Ishida, H. *Polym. Compos.* **1987**, *8*, 57.
(3) Jones, D. P.; Leach, D. C.; Moore, D. R. *Polymer* **1985**, *26*, 1385.
(4) Seferis, J. C. *Polym. Compos.* **1986**, *7*, 158.
(5) Lee, Y. Physical Properties of Poly(ether ether ketone). Ph.D. Dissertation, University of Massachusetts at Amherst, 1988.
(6) Lee, Y.; Porter, R. S. *Polym. Eng. Sci.* **1986**, *26*, 633.
(7) Lee, Y.; Lefebvre, J.-M.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 795.
(8) Lee, Y.; Porter, R. S. *Macromolecules* **1987**, *20*, 1336.
(9) Blundell, D. J.; Osborn, B. N. *Polymer* **1983**, *24*, 953.
(10) Blundell, D. J. *Polymer* **1987**, *28*, 2248.
(11) Cheng, S. Z. D.; Cao, M. Y.; Wunderlich, B. *Macromolecules* **1986**, *19*, 1868.
(12) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1980; Vol. 3.
(13) Lovering, E. G.; Wooden, D. C. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1639.
(14) Samuels, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1417.
(15) Prest, W. M., Jr.; Luca, D. J.; *J. Appl. Phys.* **1975**, *46*, 4136.
(16) Briber, R. M.; Thomas, E. L. *Polymer* **1985**, *26*, 8.
(17) Edwards, B. C. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1387.
(18) Holdsworth, P. J.; Turner-Jones, A. *Polymer* **1971**, *12*, 195.
(19) Roberts, R. C. *J. Polym. Sci., Polym. Lett. Ed.* **1970**, *8*, 381.
(20) Roberts, R. C. *Polymer* **1969**, *10*, 117.
(21) Alfonso, G. C.; Pedemonte, E.; Ponzetti, L. *Polymer* **1979**, *20*, 104.
(22) Lemstra, P. J.; Kooistra, T.; Challa, G. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 823.
(23) Boon, J.; Challa, G.; Van Krevelen, D. W. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1791.
(24) Mandelkern, L.; Allow, A. L. *J. Polym. Sci., Polym. Lett. Ed.* **1966**, *4*, 447.
(25) Bair, H. E.; Salovey, R.; Huseby, T. W. *Polymer* **1967**, *8*, 9.
(26) Jaffe, M.; Wunderlich, B. *Kolloid Z. Z. Polym.* **1967**, *216*, 203.
(27) *Annual Book of ASTM Standards*; American Society for Testing and Materials: Philadelphia, 1979; Designation D 1505-68.
(28) Harrison, I. R.; Runt, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 321.
(29) Crist, B. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 635.
(30) Crist, B.; Morosiff, N. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1023.
(31) Blundell, D. J.; Beckett, D. R.; Willcocks, P. H. *Polymer* **1981**, *22*, 704.
(32) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, A. I. M. *Polym. Commun.* **1984**, *25*, 175.
(33) Kumar, S.; Anderson, D. P.; Adams, W. W. *Polym. Commun.* **1986**, *27*, 329.
(34) Rueda, D. R.; Ania, F.; Richardson, A.; Ward, I. M.; Balta-Calleja, F. J. *Polym. Commun.* **1983**, *24*, 258.
(35) Wakelyn, N. T. *Polym. Commun.* **1984**, *25*, 306.
(36) Wakelyn, N. T. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 25.
(37) Fratini, A. V.; Cross, E. M.; Whitaker, R. B.; Adams, W. W. *Polymer* **1986**, *27*, 861.
(38) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.
(39) Lovinger, A. J.; Davis, D. D. *Macromolecules* **1986**, *19*, 1861.
(40) Lovinger, A. J.; Davis, D. D. *Polym. Commun.* **1985**, *26*, 322.
(41) Fischer, E. W.; Fakirov, S. *J. Mater. Sci.* **1976**, *11*, 1041.
(42) Groeninckx, G.; Reynaers, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1325.
(43) Rim, P. B.; Runt, J. P. *Macromolecules* **1984**, *17*, 1520.
(44) Rim, P. B.; Runt, J. P. *Macromolecules* **1983**, *16*, 762.
(45) Arakawa, T.; Nagatoshi, F.; Arai, N. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 115.