Crystallinity of Poly(aryl ether ether ketone) by Vibrational Spectroscopy

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ABSTRACT: Medium infrared spectroscopy has been used by several authors to obtain the degree of crystallinity of PEEK films. The IR absorption bands at 947 and 965 cm^{-1}, proposed by Jonas et al. are crystalline-sensitive. They appear as shoulders located in the neighborhood of other very intense absorption bands, and their deconvolution is difficult and sometimes hazardous for samples having a low crystallinity. In this same medium infrared region, designed hereafter as MIR, an additional band at 968 cm^{-1}, appearing as a shoulder, is reported for the first time. The absorbance of these bands at 947 and 965 cm^{-1} does not approach zero for a density equal to the amorphous density. The analysis of the far infrared (FIR) spectrum of amorphous and partially crystalline PEEK films have indicated two "crystalline-sensitive" bands at 218 and 303 cm^{-1}, one "amorphous-sensitive" band at 410 cm^{-1}, and an internal band at 272 cm^{-1}. The integrated absorbance of the crystalline and amorphous-sensitive bands have been correlated to the macroscopic density and the crystallinity of the films. The presence of crystalline- and amorphous-sensitive vibrational bands in the FIR spectrum of PEEK allows us to use the method proposed by Hendus et al. These FIR measurements have been interpreted on the basis of a two-phase model, and no experimental evidence has been observed for a third additional phase.

Introduction

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) or poly(aryl ether ether ketone) (PEEK), commercially introduced by ICI,[1] has received considerable interest over the past decade. PEEK is a semicrystalline polymer with an unusual combination of properties such as high chemical resistance and excellent thermal stability as well as good mechanical properties. Taking into account its high strength characteristics and melt processability, PEEK is generating interest in applications such as reinforced composites,[2] coatings, electrical connectors...[3] Considerable progress has been made toward understanding the structure and properties of PEEK, including X-ray diffraction analyses,[4-12] solution properties and molecular weight determinations,[1,13] overall crystallization kinetics,[14-16] crystallization from solution,[17-19] and thermodynamic properties of its crystalline phase.[20]

The determination of the degree of crystallinity of semicrystalline polymers is of large interest. The medium infrared region (4000–400 cm^{-1}) has been widely used to study the crystallinity of polymers because observed differences in their vibrational spectrum[21-23] could indeed be related to crystallinity, as determined by X-ray diffraction, differential scanning calorimetry, and density measurements. The examination of the medium infrared spectrum of a semicrystalline polymer generally shows that, with increasing crystallinity, vibrational bands arising from molecular units which are in the correct conformation to enter the crystalline domains become sharper and more intense, while bands due to noncrystallizable conformers decrease in intensity. As the molecular units in the amorphous regions may experience a large number of environments with slightly different vibration frequencies, they usually appear as broad bands in the infrared spectrum. The medium infrared spectroscopy has been used to determine the crystallinity of unoriented PEEK samples.[24-26] As quoted by Willis et al.,[27] "what is being observed in the vibrational spectrum is the presence of particular rotational conformers of the macromolecule which can exist in the crystal phase or/and in the amorphous region". Infrared bands which show a splitting due to the symmetry of the unit cell, such as in the case of polyethylene,[28] are the only exception to such a general rule. The crystallinity of a polymeric sample is essentially concerned with the conformation and the packing of chains and the interactions between neighboring chains. It is well-known that the vibrations observed in the FIR spectrum (below 600 cm^{-1}) are more sensitive to modifications in the conformation of the chains (bending and torsion modes). The vibrations characteristic of the molecular packing of the polymer chains appear below 500 cm^{-1}. Therefore, the investigation of the FIR spectrum is of high interest to study the crystallinity of PEEK films.

In the first part of this work, the experimental difficulties met in the determination of the crystallinity of PEEK films from their medium infrared spectrum are underlined. The main part of this work is devoted to the analysis of the far infrared spectrum of PEEK in order to correlate the integrated absorbance of some typical FIR vibrational bands to the density and the degree of crystallinity. Two vibrational bands at 218 and 303 cm^{-1} are characteristic of the crystal and one vibrational band at 410 cm^{-1} is characteristic of amorphous PEEK as indicated in a preliminary work.[29]

Experimental Section

Amorphous PEEK films with thicknesses of 25 and 260 μm obtained from ICI were used as received for MIR and FIR measurements, respectively. Partially crystalline PEEK samples were prepared by annealing amorphous films in a Mettler hot stage (type FP84). The density of the PEEK films was determined by the flotation method. Aqueous solutions of calcium nitrate were used. The density of the solutions was measured with a specific gravity meter (Mettler DA110) to within an accuracy of 0.001 g cm^{-3} at 25 °C.

The MIR and FIR measurements were performed on a Bruker IFS 113V Fourier transform infrared spectrometer with a resolution of 1 cm^{-1}. A lot of 32 interferograms was collected for

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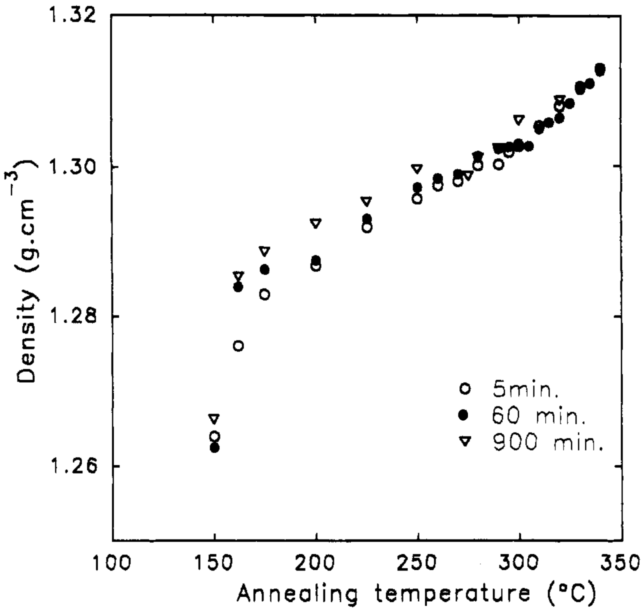

Figure 1. Density of 260 μm thick PEEK films versus the annealing temperature for annealing times of 5, 60, and 900 min.

each spectrum. The deconvolution method used to obtain the integrated absorbance from the experimental vibrational spectrum was based on a Levenberg-Marquardt algorithm[30] with lorentzian functions for crystalline bands and gaussian functions for the other bands. The integrated absorbance of the different bands has been corrected for the thickness of the film. The error on these corrected absorbances has been evaluated by using the standard deviation of the curve parameters given by the fitting process.

Results and Discussion

Figure 1 shows the variation of the density of PEEK films with respect to the annealing temperature for three different annealing times (5, 60, and 900 min). Concerning the time of annealing, no difference is noted in the density of the samples annealed during 5, 60 and 900 min in the temperature range of 300 to 340 °C. Long annealing times (900 min) lead to noticeable differences in the density of samples annealed in the temperature range of 160 to 250 °C. The three sets of data exhibit two breaks: the first break occurs around 160 to 170 °C, i.e. some 20 °C above the glass transition temperature, which corresponds to the crystallization process. The second break becomes apparent at crystallization temperatures above 300 °C. This last break could be related to modifications in morphology occurring around 300 °C in PEEK spherulites crystallized from the melt.[31] The increase of birefringence observed at high crystallization temperatures may indeed be consistent with Lovinger's findings of lamellae becoming increasingly broader.[32] Cheng et al.[20] have observed from DSC measurements that at approximately 300 °C, a third phase called the "rigid amorphous" phase falls off to zero. Optical, calorimetric, and X-ray investigations are in progress to explain these two breaks in the curve of the density versus the annealing temperature and to relate or not the upper break to the disappearance of rigid-amorphous material in the partially crystalline samples obtained by annealing of amorphous PEEK films.

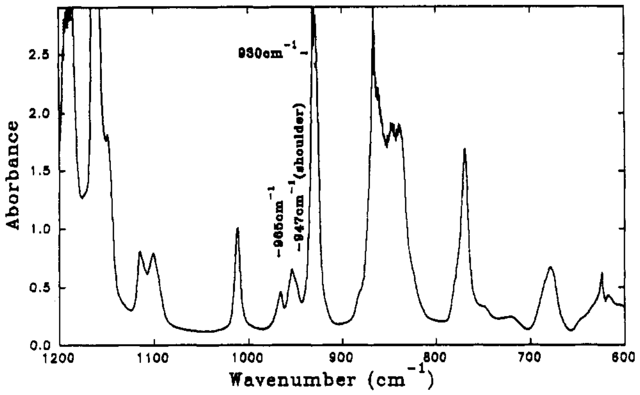

Figure 2. MIR spectrum of amorphous PEEK crystallized and annealed at 320 °C during 60 min. The absorption bands used for determination of crystallinity are shown by arrows.

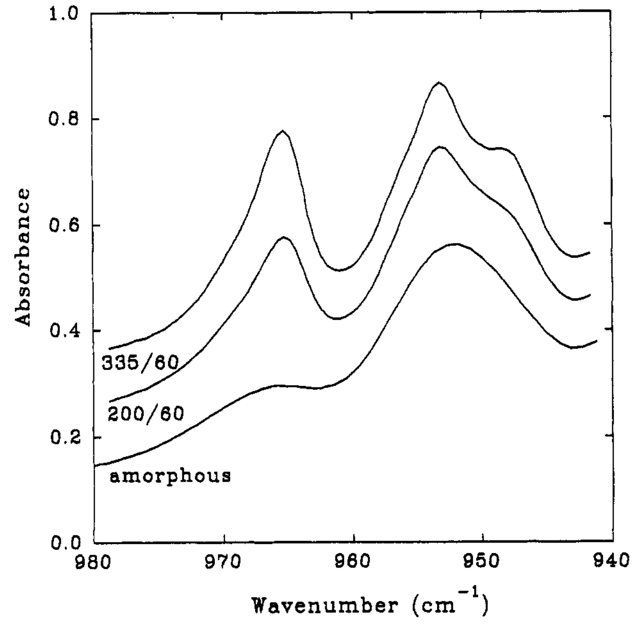

Figure 3. MIR spectra of amorphous PEEK and amorphous PEEK annealed at 200 °C and 335 °C. The annealing time is 60 min. The FTIR spectra of the annealed films have been shifted in absorbance for the presentation; the absorbance scale is the same for the three spectra.

Chalmers et al.,[24] Cebe et al.,[25] and Jonas et al.[26] have reported the observation of a crystallinity effect in the MIR region. They considered that the IR bands observed at 947 and 965 cm^{-1} were fully crystalline-sensitive. Figure 2 defines the region of interest in the enlarged part of the MIR spectrum of one typical sample. Figure 3 shows the part of the IR spectra obtained for an amorphous sample and two samples annealed from the glassy state at 200 °C and 335 °C during 60 min. It can be observed that the 947 and 965 cm^{-1} MIR bands are crystalline-sensitive as proposed by Jonas et al.[26] The deconvolution of the 980–940 cm^{-1} part of the spectra was done by considering four MIR bands located at 947, 953, 965, and 968 cm^{-1}. Figure 4 shows the deconvolution of the part of the IR spectrum relative to the sample annealed at 200 °C during 60 min. A fourth absorption band at 968 cm^{-1} appearing as a shoulder to the asymmetric absorption band at 965 cm^{-1} was taken into account in our deconvolution treatment. This shoulder at 968 cm^{-1} had not been yet reported. We don't succeed in deconvoluting the spectral region from 900 to 980 cm^{-1} including the peak at 930 cm^{-1} with an absorbance always larger than 2.5. The deconvolution was carried out over a narrower spectral range, and even with such a procedure, it was impossible to deconvolute the MIR spectra for samples annealed in the temperature range of 150 and 175 °C. Figure 5 shows the integrated absorbance of the two MIR bands at 947 and 965 cm^{-1} versus the density of the films. A linear dependence of the integrated absorbance with respect to the density is observed as already reported by other authors,[24-26] but the extinction of these bands does not occur for a density value equal to the amorphous density ρ_a. The values

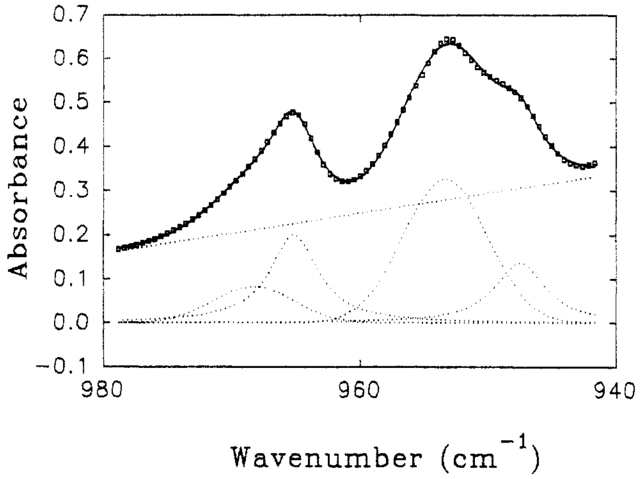

Figure 4. Deconvolution of the MIR spectrum of the sample annealed at 200 °C during 60 min. Fitted curve: solid line; experimental data: □.

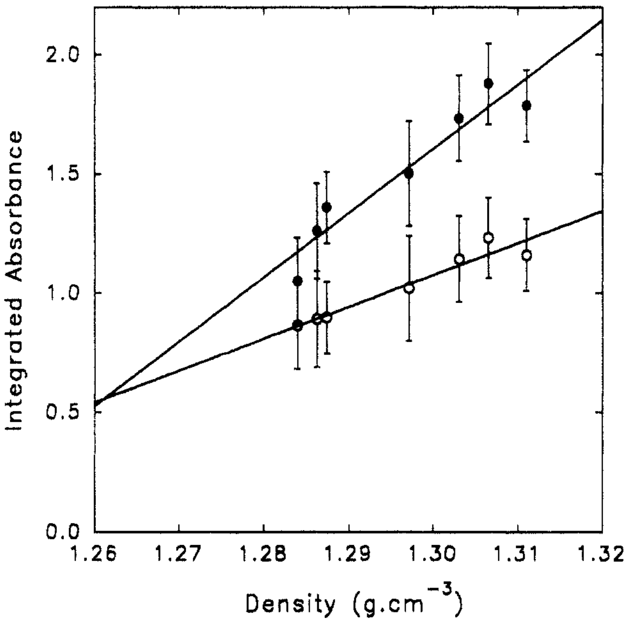

Figure 5. Integrated absorbance of "crystalline" bands at 947 (○) and 965 cm^{-1} (●) versus the density of the PEEK film. Error bars correspond to ±2 standard deviations.

reported for the amorphous density are in the range of 1.260 to 1.267 g cm^{-3}.[14,25,34-36] At least two explanations can be proposed in order to explain why the extinction of these bands does not occur for a density value equal to the amorphous density. The first explanation is relative to the deconvolution process itself. Secondly, as suggested by several authors, PEEK can locally adopt, in the amorphous state, some conformations occurring on a larger scale in the crystal. This implies that the 947 cm^{-1} vibration may be not a fully crystalline-sensitive band. This small contribution to the MIR spectrum of PEEK underlies the difficulty met in the treatment of absorption bands, i.e. the difficulty to deconvolute quantitatively an absorption band appearing as a shoulder near a very strong vibrational band.

A preliminary study[29] has shown that the FIR spectrum of PEEK containing torsion and lattice modes of vibration seems to be a convenient approach to the determination of the crystallinity.[27] Figure 6 shows the FIR spectra of amorphous PEEK (a), PEEK annealed during 60 min at 225 °C (b), and at 330 °C (c). It can be seen that some vibrations are crystalline- or amorphous-sensitive. The absorbance of the bands at 218 and 303 cm^{-1} increases with annealing temperature and these bands could be considered as "crystalline"-sensitive absorption bands. The vibrational band at 272 cm^{-1} seems to be independent on the annealing temperature and therefore on the crystallinity. On the other hand, as the absorbance of the FIR absorption band at 410 cm^{-1} decreases with increasing annealing temperature, this band could be considered as an "amorphous"-sensitive band. In order to analyze quantitatively the FIR spectra, the different absorption bands of this region have been deconvoluted following the same procedure as used for the MIR region. Figure 7a–c shows the deconvolution of the FIR spectra given in Figure 6.

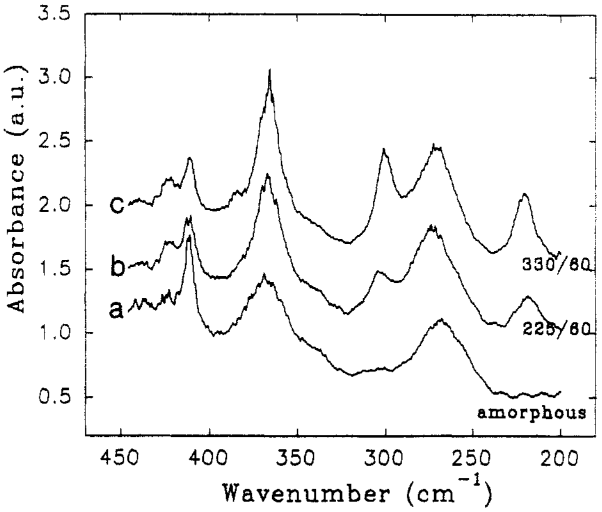

Figure 6. Far infrared spectra of amorphous PEEK film, partially crystalline PEEK films obtained by annealing of amorphous films at 225 °C and at 330 °C. The annealing time is 60 min. The FTIR spectra of the annealed films have been shifted in absorbance for the presentation; the absorbance scale is the same for the three spectra.

The residual R of the absorption band at 272 cm^{-1} has been plotted versus the density of the PEEK films (Figure 8). The residual R is defined as $R = 100 \times (A_{272} - \langle A_{272}\rangle)/\langle A_{272}\rangle$ where A_{272} and $\langle A_{272}\rangle$ are the integrated absorbance of the band at 272 cm^{-1} and its mean value on all investigated samples, respectively. The values of the residual R do not show any systematic modification with respect to the density of the films but are randomly distributed around zero. It can be concluded that the integrated absorbance of the FIR band at 272 cm^{-1} does not depend on the thermal treatment of the PEEK films. This band will be used to normalize the absorbance measurements of the bands at 218, 303, and 410 cm^{-1}.

The integrated absorbance of the bands at 218, 303, and 410 cm^{-1}, corrected for the thickness of the films, has been plotted versus the density of the films (Figure 9a,b). A linear dependence of the integrated absorbance versus the density of the samples is observed for the bands at 218 and 410 cm^{-1}. The following relationships are obtained:

$$A_{218} = 182.4\langle\rho\rangle - 229.8$$

$$A_{410} = -35.2\langle\rho\rangle + 48.75$$

The extinction of the assumed FIR crystalline-sensitive bands corresponds to 1.260 g cm^{-3} (Figure 9a), a value in good agreement with the measured density of amorphous PEEK sample.[14,25,33-36] The extinction of the assumed FIR amorphous-sensitive band corresponds to 1.385 g cm^{-3} (Figure 9b), a value in agreement with the crystal density of 1.394 g cm^{-3} obtained from a refinement of the crystal structure of PEEK in the orthorhombic unit cell.[5,12]

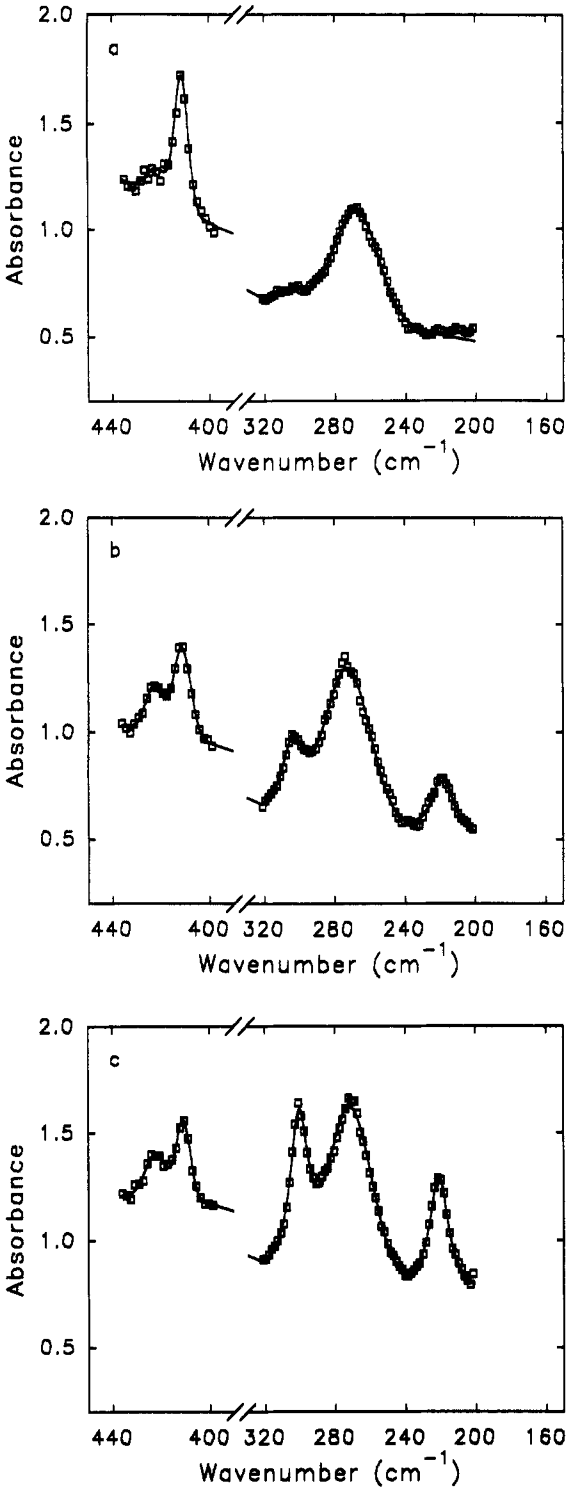

Figure 7. Deconvolution of the three FIR spectra given in Figure 6. Fitted curve: solid line; experimental data: □.

Drawing a straight line through all the data relative to the vibrational band at 303 cm^{-1} could be questioned as suggested by a referee. Let us note that the linear least squares fitting gives the same deviation (5%) on the parameters of all the three "mean best" lines for the three vibrational bands. Moreover, a small broad peak is present in the FIR spectrum of amorphous PEEK in the range of 295 to 320 cm^{-1} (Figure 6) and in the deconvoluted spectrum (Figure 7a). Let us note that differences have been observed between the heats of crystallization and melting of quenched amorphous PEEK samples.[34,35] These differences have been attributed to a residual crystallinity produced during quenching. A small fraction of crystalline material could be present in the so-called amorphous starting films. The small broad peak around 303 cm^{-1} could be the contribution of this small fraction of crystalline material. In this case, an experimental value

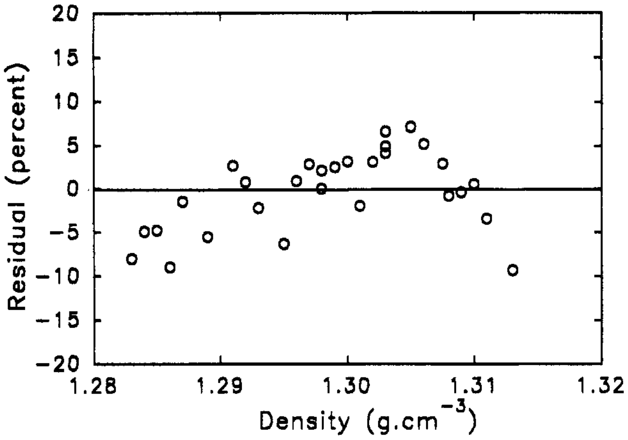

Figure 8. Residual R of the integrated absorbance of the vibrational band at 272 cm^{-1} versus the annealing temperature.

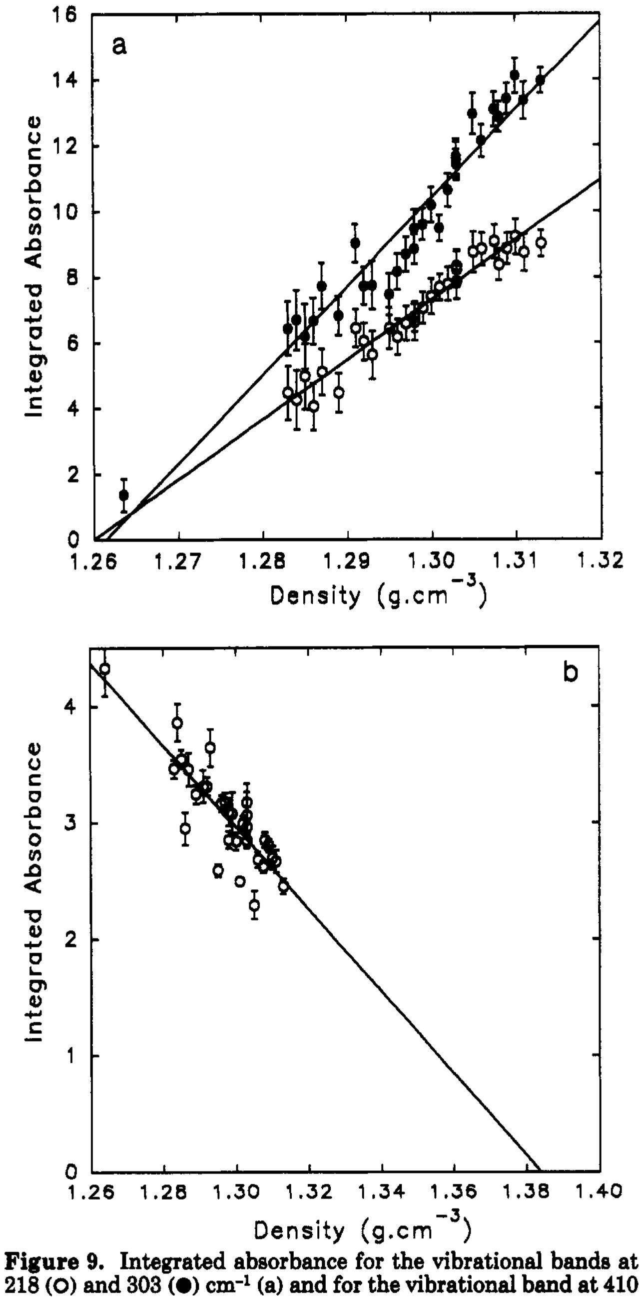

Figure 9. Integrated absorbance for the vibrational bands at 218 (○) and 303 (●) cm^{-1} (a) and for the vibrational band at 410 cm^{-1} (b) versus the density of the PEEK films annealed for 5, 60 and 900 min. Error bars correspond to ±2 standard deviations.

of the integrated absorbance is available for only one sample having a very low degree of crystallinity. With error bars equal to two standard deviations, this last result can be taken into account by the straight line obtained by a least squares fitting on all data. The following relationship is obtained:

$$A_{303} = 269.3\langle\rho\rangle - 339.7$$

The extinction of the assumed FIR crystalline-sensitive band at 303 cm^{-1} corresponds to 1.261 g cm^{-3} (Figure 9a), a value also in agreement with the value determined from the FIR band at 218 cm^{-1} and the reported value for the density of amorphous PEEK.

The two-phase model has been used by several authors[10,14,33] to determine the crystallinity of PEEK. In this hypothesis, the following data are needed to obtain the degree of crystallinity: the macroscopic density $\langle\rho\rangle$, the densities of amorphous (ρ_a), and crystalline PEEK (ρ_c). The values reported for ρ_a are in the range of 1.260 to 1.267 g cm^{-3}.[14,25,34-36] The density of crystalline PEEK is obtained from the volume of the "mean" crystallographic unit cell. Several authors have determined the variation of the crystal density of PEEK versus the annealing temperature or the crystallization temperature.[9-11] We have realized some measurements of the crystal density of annealed stretched PEEK films. The wide angle X-ray pattern of such samples contains some 18 diffraction spacings that have been used in the fitting. These values[37] of the crystal density do not show any substantial modification with respect to the annealing temperature and are very similar to the values reported by Fratini et al.[5] and Iannelli.[12] We have used the values of 1.261 and. 1.385 g cm^{-3} for the density of the amorphous and crystalline PEEK, respectively. These values have been obtained from the extrapolation of measurements on FIR bands (Figure 9a,b).

In order to check if the absorption bands at 218, 303, and 410 cm^{-1} in the FIR spectrum of PEEK films are crystalline- or amorphous-sensitive bands, two procedures have been used. (a) When crystalline and amorphous bands are present simultaneously in the vibrational spectrum, Hendus et al.[38] have shown that a linear relationship is existing between the ratio of the extinction coefficients of a crystalline and an amorphous band and the degree of crystallinity (volume crystallinity v_c). The relation $v_c = D/[D + K/A]$ has been rewritten as $(1 - v_c) D = (K/A)v_c$. K and A are the molar extinction coefficients for amorphous and crystalline samples and D is the ratio of the absorbances of crystalline and amorphous bands. The data $(1 - v_c)A_{218}/A_{410}$ for the crystalline band at 218 cm^{-1} and $(1 - v_c)A_{303}/A_{410}$ for the crystalline band at 303 cm^{-1} have been plotted versus the volume crystallinity v_c (Figure 10a,b). For each value of the integrated absorbance for the bands at 218, 303, and 410 cm^{-1}, the error bars corresponding to ±2 standard deviations of the parameters of the curve fitting have been drawn. The two relationships obtained from a least squares fitting are

$$(1 - v_c)A_{218}/A_{410} = -0.3225 + 0.0720v_c$$

$$(1 - v_c)A_{303}/A_{410} = -0.643 + 0.1082v_c$$

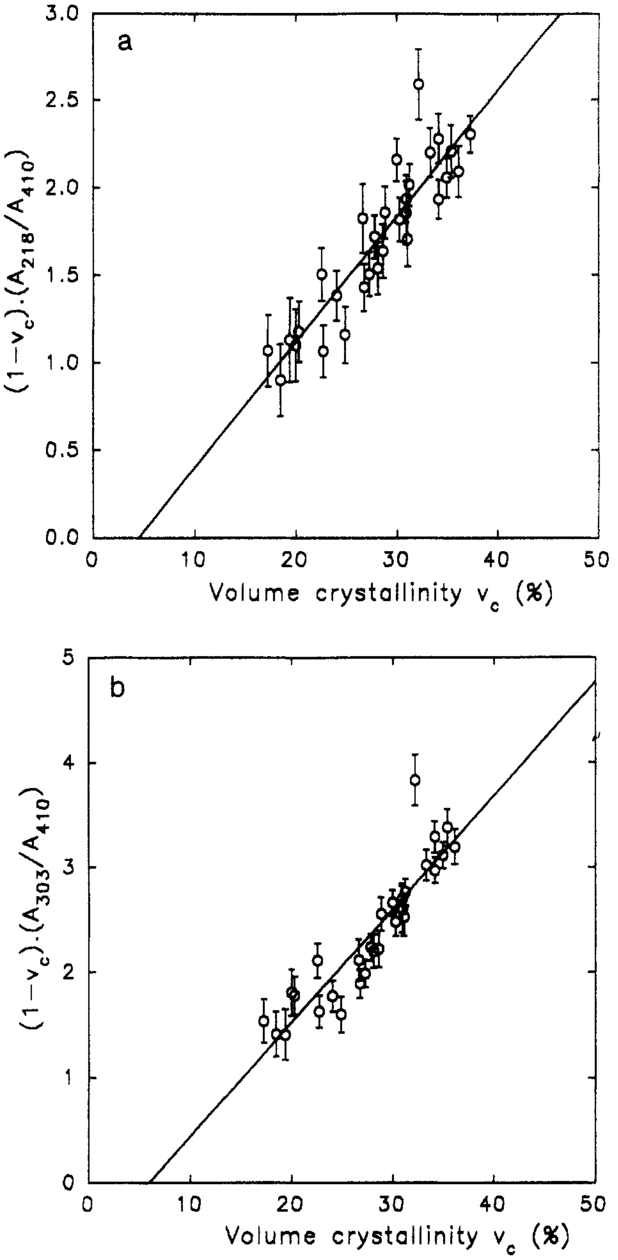

Figure 10. Hendus's plot for the vibrational bands at 218 cm^{-1} (a) and at 303 cm^{-1} (b). Error bars correspond to ±2 standard deviations.

The two extrapolated values give a value of the degree of crystallinity equal to 0.05 in place of zero as expected for fully crystalline- and amorphous-sensitive vibrational bands. The main reason for this small deviation is the lack of several samples having a crystallinity in the range of 0 to 15%. (b) A second way to obtain the degree of crystallinity from the FIR measurements is the following. The integrated absorbances of the bands at 218, 303, and 410 cm^{-1} have been normalized with respect to the band at 272 cm^{-1}. These integrated absorbances are plotted versus the weight degree of crystallinity, calculated from density measurements (Figure 11a,b). The following relationships are obtained:

$$A_{218} = 0.056 + 0.0081w_c$$

$$A_{303} = 0.028 + 0.0130w_c$$

$$A_{410} = 0.203 - 0.0022w_c$$

Figure 11, parts a and b, show that the 218 and 303 cm^{-1} FIR bands are characteristic of crystalline PEEK and that the 410 cm^{-1} FIR band is characteristic of amorphous PEEK, respectively. Using the normalizing process given here above, these three FIR absorption bands allow determination of the crystallinity of PEEK from the relationships given above.

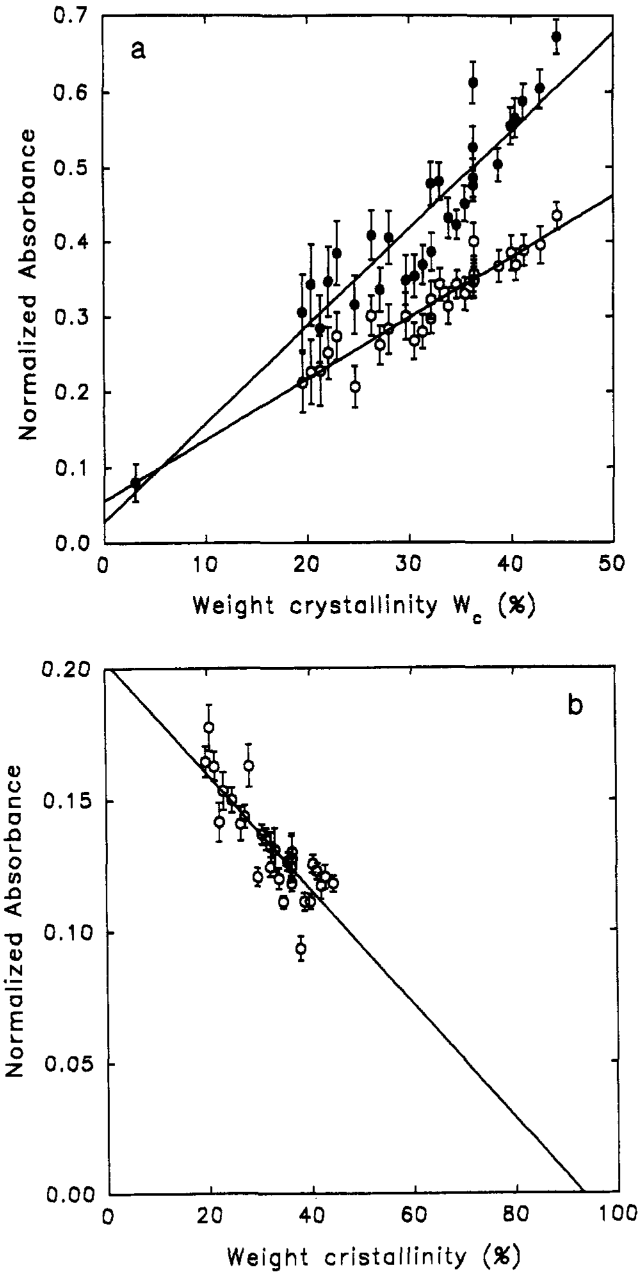

Figure 11. Normalized integrated absorbance for the vibrational bands at 218 (○) and 303 (●) cm^{-1} (a) and the band at 410 cm^{-1} (b) versus the weight degree of crystallinity. Error bars correspond to ±2 standard deviations.

Conclusions

The analysis of the absorption bands at 947and 965 cm^{-1} in the medium infrared spectrum of PEEK shows the difficulty in determining the degree of crystallinity from MIR bands. Two suggestions have been proposed in order to explain the deviation of the two MIR crystalline bands: firstly, the precision of the deconvolution process; secondly, the presence of conformers in the amorphous regions similar to that in the crystalline regions but on a lower scale. Indeed the absorbance of these vibration bands does not reach zero for a density equal to the amorphous density. In the far infrared region, the two absorption bands at 218 and 303 cm^{-1} and the band at 410 cm^{-1} are characteristic of the crystalline and the amorphous phases, respectively. The absorption band at 272 cm^{-1} is independent of the crystallinity of the PEEK films and can be used to normalize the measurements of absorbance. Two procedures have been used to obtain the degree of crystallinity of PEEK from FIR measurements: (a) Hendus's method where the ratio of the integrated absorbance of a crystalline band (218 and 303 cm^{-1}) and an amorphous band (410 cm^{-1}) is plotted versus the volume degree of crystallinity calculated from the macroscopic density measurements. The linear relationship obtained justifies the attribution of these three vibrational bands; (b) the integrated absorbances of these three FIR bands show a linear relation with respect to the weight degree of crystallinity.

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