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Polymer Vol. 36 No. 22, pp. 4209–4213, 1995

0032-3861/95/$10.00+0.00

A study of the absorption of chlorinated organic solvents by poly(ether ether ketone) using vibrational spectroscopy

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(Received 22 December 1994)

A study of the effects of some chlorinated organic solvents on the physical and spectral properties of poly(ether ether ketone) (PEEK) has been carried out. Infra-red and Raman spectroscopy, as well as mass diffusion studies, were used to examine the consequences of exposing PEEK to carbon tetrachloride, methylene chloride, chloroform and tetrachloroethane. Certain solvents were found to cause swelling and induce crystallization in the polymer. The effects of these solvents on the Raman spectrum of PEEK allowed a fictive temperature of 250°C to be assigned. Lewis acid–base theory was used to interpret the different swelling effects.

(Keywords: poly(ether ether ketone); chlorinated organic solvents; diffusion studies)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a thermoplastic polymer with useful high-temperature properties that make it attractive as an engineering polymer, particularly in the areas of bearing materials and composites[1]. One particularly important property of PEEK has been its apparent chemical inertness[2]. However, recent studies have observed that some solvents, including methylene chloride, chloroform, toluene and chlorophenol, are absorbed by PEEK, causing plasticization and inducing crystallization in the polymer[3–7]. A preliminary study reported by our laboratories demonstrated that 1,1,2,2-tetrachloroethane (TCE) is absorbed by PEEK to an extraordinary degree not formerly reported in studies of other organic solvents[8]. The phenomenon of plasticization may have a serious effect on the applicability of the polymer in engineering, so an understanding of the absorption mechanism and the ability to predict solvent behaviour is of obvious importance.

Vibrational spectroscopy has been applied in a number of other studies of PEEK. The infra-red spectrum of PEEK was reported by Nguyen and Ishida[9] and an attempt was made to differentiate between the crystalline and amorphous contributions to the spectrum. Infra-red spectroscopy has also been used to examine the crystallization and melting behaviour of PEEK[10–12]. Chalmers and coworkers[10] used reflection infra-red spectroscopy and X-ray scattering to investigate the percentage crystallinity of PEEK. They were able to correlate the intensity changes of certain bands with the crystallinity values determined by wide-angle X-ray scattering. Fourier-transform (*FT*) Raman spectroscopy has also been used in recent studies of PEEK[13–16] and has also been used previously as a means of investigating the thermally induced and solvent-induced plasticization of PEEK[8,13,14]. These studies demonstrated that the presence of the solvent induces additional molecular mobility, and the mechanical characteristics of the polymer appear similar to those of the polymer at some high temperature.

In the present study we examine the effect of various chlorinated organic solvents on PEEK using both Fourier-transform infra-red (*FT* i.r.) and *FT*-Raman spectroscopy. These techniques provide a useful means of determining the solvent-induced and thermally induced crystallinity of PEEK. A fictive temperature, a means of comparing solvent and thermal effects, is also determined for the solvated polymer. Each solvent studied affects PEEK to varying degrees, and this variation is explained using Lewis acid–base theory.

EXPERIMENTAL

Polymer samples were supplied by ICI Materials, Wilton, UK. To produce amorphous PEEK, samples were heated to 400–420°C then quenched in liquid nitrogen before use. Samples of amorphous PEEK were exposed to solvent in sealed containers at room temperature for 24 h prior to examination. Chloroform, TCE, methylene chloride and carbon tetrachloride

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(Aldrich) were all analytical grade and used without further purification.

The absorption experiments were carried out by immersing the polymer samples (dimensions ca. 10 mm × 30 mm, thickness 0.25 mm) in the solvent in sealed containers maintained at room temperature. After the appropriate time interval the samples were removed from the containers, blotted dry and weighed on an analytical balance. After weighing, the samples were immediately returned to the containers.

All the *FT*-Raman spectra were recorded using a Bomem Ramspec 152 equipped with an indium gallium arsenide (InGaAs) photodiode detector and using 1.05 W of 1064 nm radiation from a Quantronix Series 100 Nd:YAG laser. For each spectrum 100 scans were co-added, apodized with a cosine function and Fourier-transformed to give a resolution of 4 cm^{-1}. The spectral contribution of the solvent was removed by subtraction of the spectrum of the pure solvent. The relative intensities of the bands in each spectrum were calculated with respect to the intensity of the band at 1595 cm^{-1}. This mode was chosen as a reference because it has been shown to be relatively insensitive to changes in environment[13]. For the temperature study the sample (dimensions ca. 10 mm × 10 mm, thickness 0.5 mm) was mounted into the hot stage of a Linkam THMS 600 temperature cell. The sample was allowed to equilibrate at the appropriate temperature for 10 min before scanning.

All the infra-red spectra were recorded using a Bomem Ramspec 152 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. A Spectratech Contact Sampler attenuated total reflectance cell with a ZnSe crystal of angle 45° was used. For each spectrum, 200 scans over the frequency range 5000–400 cm^{-1} were co-added, apodized with a cosine function and Fourier-transformed to give a resolution of 4 cm^{-1}. The spectral contribution of the solvent was removed by subtraction of the infra-red spectrum of the pure solvent.

RESULTS AND DISCUSSION

Diffusion studies

The uptake of various chlorinated organic solvents by amorphous PEEK was examined. *Table 1* lists the percentage weight increase observed for amorphous PEEK on exposure to various chlorinated solvents for 24 h at room temperature. While there is a significant uptake of solvent in the cases of methylene chloride, chloroform and TCE, there is no mass increase in the case of carbon tetrachloride. These results are in general agreement with earlier studies of solvent uptake by PEEK. Hay and Kemmish[5], Stober *et al.*[3] and Wolf *et al.*[17] all examined the equilibrium mass uptake of chloroform by PEEK, and these studies reported values of 55, 59 and 51%, respectively. Stober *et al.* and Hay and Kemmish also found no uptake by carbon tetrachloride. There is more discrepancy among those results obtained for methylene chloride. Grayson and Wolf[4] found that PEEK showed a 22% mass increase due to the presence of methylene chloride, while another study by Stober *et al.*[3] obtained a higher value of 32%. The current study obtained a value of 33%, in agreement with the latter study. Clearly TCE has the most dramatic effect on PEEK, causing a weight increase of 265%. Time-dependent studies of the mass uptake by PEEK of methylene chloride, chloroform and TCE produced data consistent with a Fickian diffusion process[8].

It was noted that on immersion in methylene chloride, chloroform and TCE, the clear amorphous PEEK becomes opaque in appearance like the crystalline material. The polymer remains clear on immersion in carbon tetrachloride. These observations indicate that crystallization occurs during exposure to methylene chloride, chloroform and TCE and no crystallization is induced by the presence of carbon tetrachloride.

Table 1 The percentage weight increase of amorphous PEEK after 24 h exposure at room temperature to various chlorinated aliphatic hydrocarbons

Solvent	Weight increase (%)
Carbon tetrachloride	0 ± 0
Methylene chloride	33 ± 4
Chloroform	52 ± 3
Tetrachloroethane	265 ± 10

Raman studies

The Raman bands of PEEK have been assigned in several recent studies and are discussed in detail elsewhere[13,15,16]. *FT*-Raman spectra of both crystalline and amorphous PEEK used in the current study are shown in *Figure 1*. The *FT*-Raman spectra of PEEK after the amorphous polymer was exposed to various chlorinated organic solvents were also recorded. A shift in frequency was observed to the C=O stretching mode in most cases (*Figure 2*). While the C=O stretching mode appears at 1651 cm^{-1} in the untreated amorphous spectrum, it shifts to lower frequencies after exposure to methylene chloride, chloroform and TCE. The carbonyl bands in these spectra are closer in frequency to the 1644 cm^{-1} band observed in the crystalline material. However, the C=O stretching mode remains unaffected when the polymer is exposed to carbon tetrachloride.

To compare thermal effects with solvent effects on PEEK, the Raman spectra of untreated amorphous

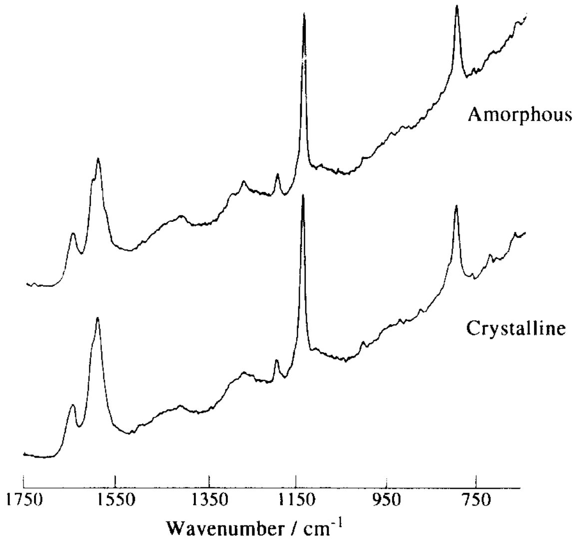

Figure 1 *FT*-Raman spectra of amorphous and crystalline PEEK

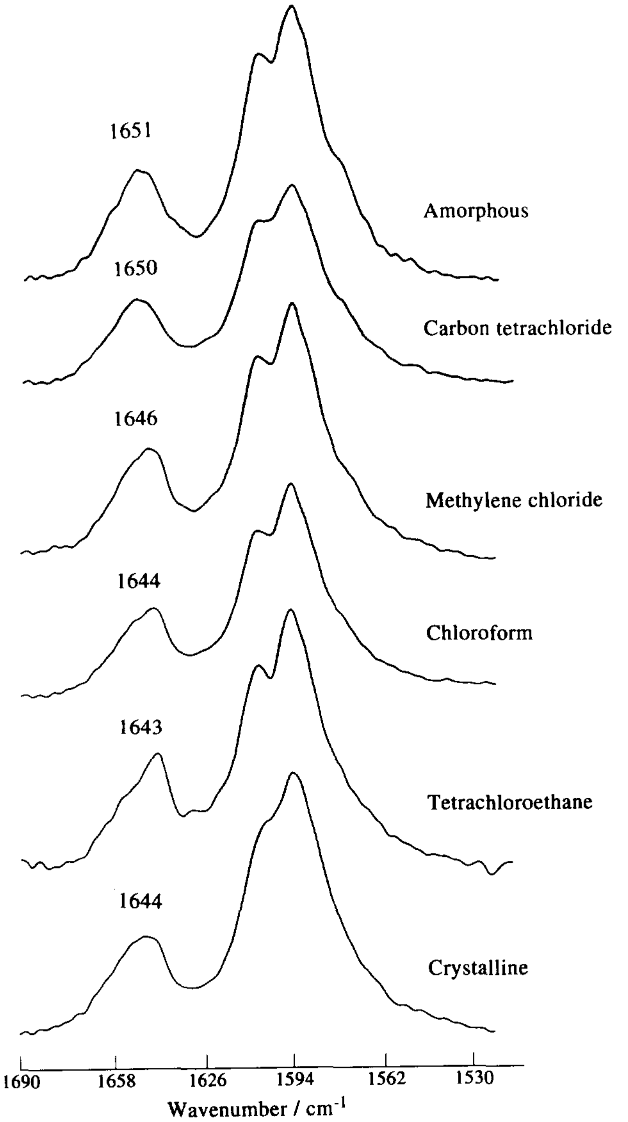

Figure 2 The carbonyl stretching region of the Raman spectra of amorphous and crystalline PEEK, and PEEK exposed to various chlorinated solvents

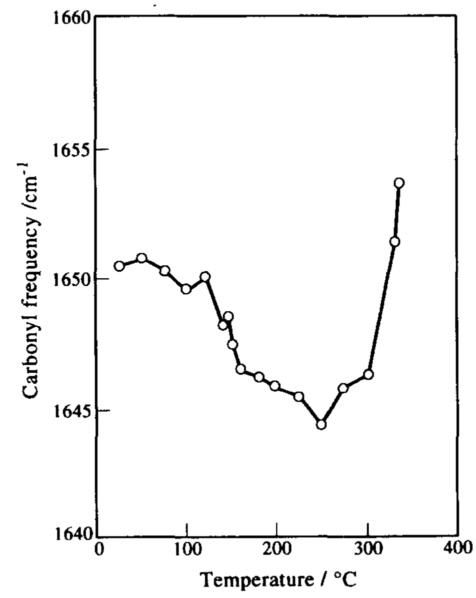

Figure 3 The frequency of the carbonyl stretching mode of PEEK as a function of temperature

PEEK over a range of temperature from ambient to melting point were also recorded. As was observed in the solvent spectra, the frequency of the carbonyl stretching mode is affected by an increase in temperature. *Figure 3* illustrates the frequency of the amorphous PEEK carbonyl mode as a function of temperature. This plot shows that, as the temperature increases, the C=O frequency gradually shifts to a lower wavenumber until it reaches 250°C, where it is observed at about 1645 cm^{-1}. There is a sharp shift after a temperature of 140°C is attained, which is in the region of T_g. After 250°C the carbonyl frequency rapidly begins to increase. These observations indicate that up to 250°C there is a gradual crystallization of the originally amorphous polymer, after which the polymer begins to melt and the spectral properties appear like those of the original amorphous material.

Infra-red studies

Attenuated total reflectance (a.t.r.) spectroscopy was the infra-red technique chosen for this study because it avoids the necessity of forming the thin films of PEEK required for transmission spectroscopy, which is difficult because of the lack of an appropriate solvent and the high T_m. The a.t.r. spectra of amorphous and crystalline PEEK are shown in *Figure 4*. Nguyen and Ishida[11,12] reported the transmission *FT* i.r. spectra of PEEK films and were able to assign the observed vibrational modes for both amorphous and crystalline phases. The current a.t.r. spectra show bands at similar frequencies. As the intensities of a.t.r. infra-red bands are wavelength-dependent, bands at lower frequencies are more intense than those observed in transmission.

The a.t.r. spectra of amorphous PEEK after immersion in various chlorinated organic solvents were recorded and are also shown in *Figure 4*. While there are only a few changes noted to the carbon tetrachloride spectrum, there are significant changes to the PEEK spectra after immersion in methylene chloride, chloroform and TCE. It was found that the intensity ratio of the 952 and 965 cm^{-1} bands was affected by the presence of methylene chloride, chloroform or TCE. The doublet was unchanged in the presence of carbon tetrachloride. The doublet with component bands at around 952 and 965 cm^{-1} was shown by Chalmers *et al.*[10] to be dependent on the crystallinity of the sample. The calculated ratios of the 952 and 965 cm^{-1} bands are summarized in *Table 2*. Based on these ratios it may be deduced that the solvents methylene chloride, chloroform and TCE induce crystallization in PEEK, while carbon tetrachloride has no effect. The intensity ratio of the 965 cm^{-1}/952 cm^{-1} bands increases with the increasing percentage crystallinity of the PEEK sample. It should be pointed out that there are differences between the 1000–1300 cm^{-1} regions of the crystalline PEEK spectrum and the methylene chloride, chloroform and TCE spectra. Bands appearing in this region are mainly associated with C–H vibrations, are heavily overlapped and changes are difficult to quantitate.

Another useful mode in the infra-red spectrum is the carbonyl band, as was found in the Raman study. *Figure 5* shows the C=O stretching mode of crystalline and amorphous PEEK. The carbonyl band is broad,

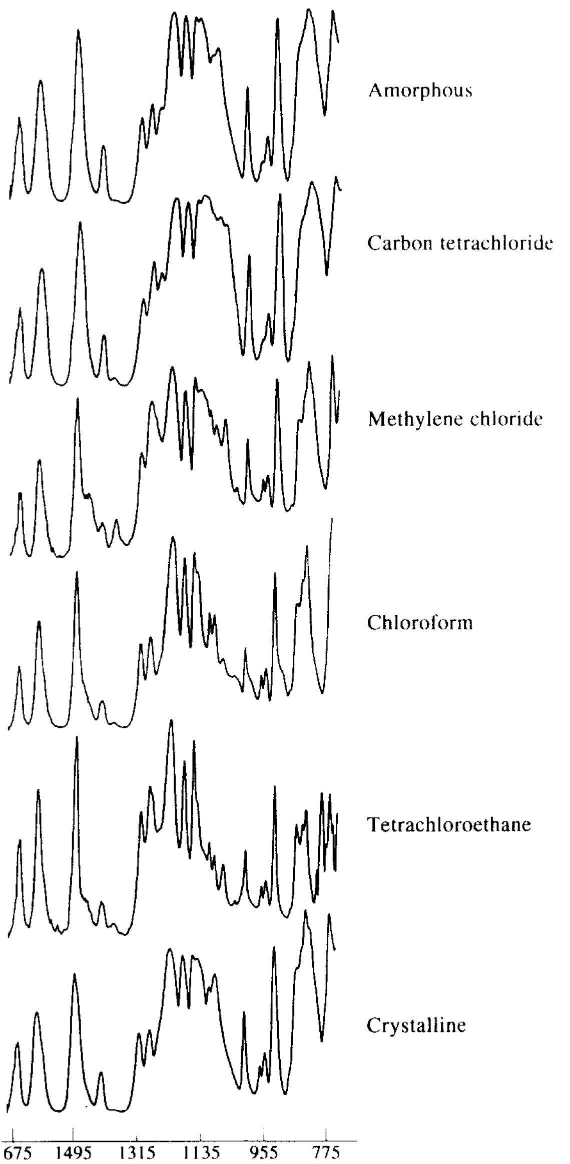

Figure 4 A.t.r. infra-red spectra of amorphous and crystalline PEEK, and amorphous PEEK exposed to various chlorinated solvents

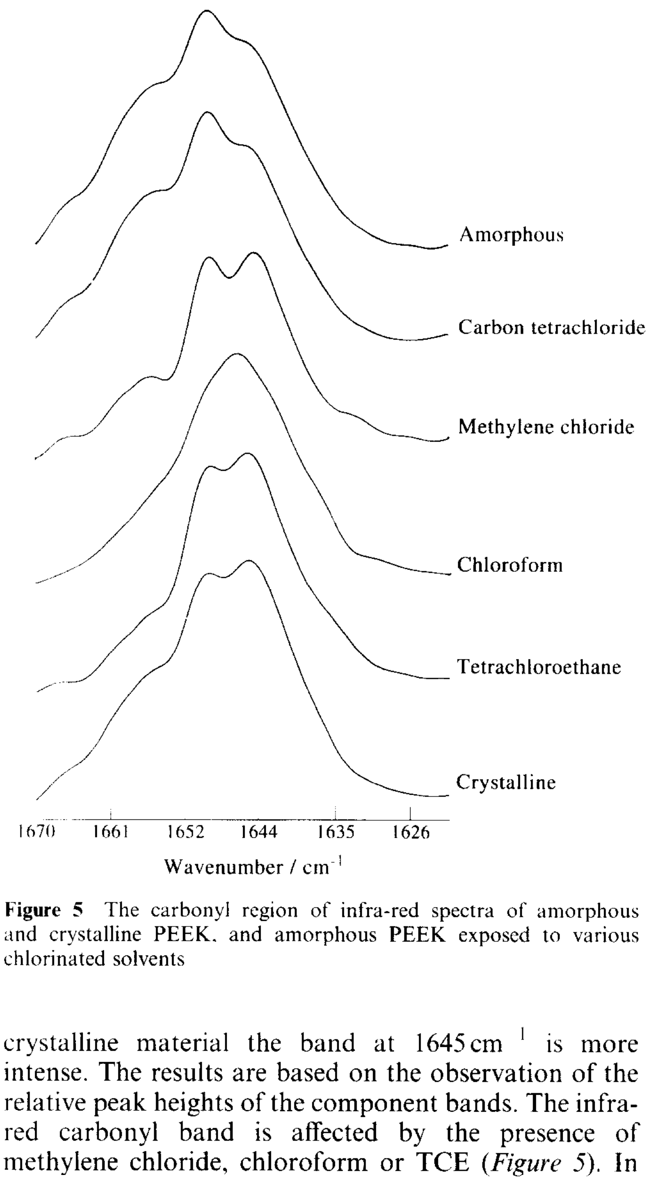

Figure 5 The carbonyl region of infra-red spectra of amorphous and crystalline PEEK, and amorphous PEEK exposed to various chlorinated solvents

consisting of several overlapping component bands. Both the amorphous and crystalline polymer show components centred at 1645, 1650, 1657 and 1666 cm^{-1}. The shoulders at 1657 and 1666 cm^{-1} appear similar in each case, but the relative amounts of the components at 1645 and 1650 cm^{-1} vary according to crystallinity. For amorphous PEEK the most intense component is observed at 1650 cm^{-1}, while in the crystalline material the band at 1645 cm^{-1} is more intense. The results are based on the observation of the relative peak heights of the component bands. The infra-red carbonyl band is affected by the presence of methylene chloride, chloroform or TCE (*Figure 5*). In the cases of methylene chloride and TCE it is clearly seen that the component at 1645 cm^{-1} has increased in intensity and the carbonyl band appears now very similar to that of the crystalline carbonyl band. In the case of chloroform the component bands are less distinct and the band heavily overlapped, but is centred at 1646 cm^{-1}, again indicating the induction of crystallinity to the originally amorphous polymer. The spectrum of PEEK after exposure to carbon tetrachloride is almost identical to that of the untreated amorphous polymer.

Table 2 The effect of various chlorinated aliphatic hydrocarbons on the infra-red intensity ratio of 965 cm^{-1}/952 cm^{-1} bands

Solvent	I_{965}/I_{952} [a]
Untreated amorphous	0.40
Carbon tetrachloride	0.38
Methylene chloride	0.63
Chloroform	0.77
Tetrachloroethane	0.81
Untreated crystalline	0.69

[a] Standard deviation: ±0.03

Discussion

The Raman results allow a useful comparison of the solvent and thermal effects on PEEK. As mentioned, a recent Raman study of PEEK showed that the technique can be used to sense the plasticization of PEEK induced thermally and with the solvent toluene[13]. That study found that the presence of toluene mimics the spectral characteristics of the unsolvated polymer at about 120°C. At that temperature the molecular movement in PEEK is associated with the ether linkages[11]. A similar approach may also be applied to the results presented here. The changed frequency values of the C=O stretching mode of PEEK in methylene chloride, chloroform or TCE correspond to the values for the unsolvated polymer at a temperature near 250°C. That is, the molecular relaxation processes observed spectroscopically for the polymer in the solvents methylene chloride, chloroform and TCE correspond to fictive temperatures of 250°C. The high fictive temperatures, well above T_g, indicate that the plasticization of PEEK through swelling by these solvents is quite extensive. Nguyen and Ishida[9] identified spectral changes in this temperature range as being associated with movement of the carbonyl linkages. That is, the polymer chains undergo a secondary viscoelastic mechanism to attain the preferred conformation so that crystallization can occur. Additionally, investigation of the symmetric C–O–C stretching mode of PEEK after exposure to TCE showed an increase in intensity of this mode corresponding to the spectrum of the unsolvated polymer at a high temperature near 240°C[8].

The spectral data and diffusion results have shown that the solvents methylene chloride, chloroform or TCE cause swelling and crystallization in PEEK. In particular, tetrachloroethane has been shown to cause dramatic swelling of PEEK, to a degree not formerly observed for any other solvents: amorphous PEEK is capable of taking up to 265% of its weight in TCE. The effect that certain chlorinated hydrocarbons have on PEEK may be explained by Lewis acid–base interactions between the polymer and the solvent. PEEK acts as a soft base due to the presence of the C=O, C–O–C and aromatic groups in the structure, which may act as electron donors. The chlorinated hydrocarbons may act as acids. The solvents affect PEEK to varying degrees and this is believed to be due to their relative acidities. The acid character of the chlorinated solvents may be determined simply by examining each of their chemical structures. The carbon tetrachloride molecule is symmetric and as such has no active site. This accounts for the fact that carbon tetrachloride has no swelling effect on PEEK. By comparison, methylene chloride, chloroform and TCE all have a hydrogen atom attached to a carbon atom with a chlorine atom (an electronegative atom) (H–C–Cl). Thus, they all have an active site. Chloroform is more acidic than methylene chloride because it has only one, rather than two, hydrogen atoms. TCE is more acidic than both chloroform and methylene chloride because it has two acidic sites per molecule.

The swelling of PEEK occurs because the interaction of a solvent with the polymer results in solution of some of the solvent in the polymer phase and solution of some of the polymer in the solvent phase. At the same time, crystallinity is induced in the polymer by the solvent. The interaction between PEEK and the chlorinated solvent causes electronic charge to be withdrawn from the C=O bond of PEEK into the polymer–solvent bond. This lowers the C=O bond force constant and causes a shift to lower frequencies of vibration of the C=O stretching mode compared to the amorphous environment.

CONCLUSIONS

Exposure of amorphous PEEK to various chlorinated aliphatic hydrocarbons was found to have considerable effects on the spectral properties of PEEK. The solvents methylene chloride, chloroform and TCE were found to cause swelling and induce crystallization in the polymer. In particular, TCE was shown to produce unusually dramatic swelling of PEEK. Lewis acid–base interaction theory has been used to rationalize why such solvents affect PEEK in this way. The above-mentioned solvents are acidic in nature and are capable of interacting with the basic sites in the PEEK molecule. *FT*-Raman spectroscopy has been applied to obtain a semi-quantitative estimation of the extent of plasticization of PEEK by chlorinated solvents. It has been shown that methylene chloride, chloroform and tetrachloroethane mimic the unsolvated polymer at temperatures in the region of 250°C.

ACKNOWLEDGEMENTS

The authors wish to thank Professor B.J. Briscoe and ICI Materials, Wilton, UK for providing the polymer samples and for financial support of B.H. Stuart.

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