Polymer Bulletin 11, 433–435 (1984)

Polymer Bulletin

Crystallinity in Poly(Aryl-Ether-Ketone) Plaques Studied by Multiple Internal Reflection Spectroscopy

J. M. Chalmers, W. F. Gaskin and M. W. Mackenzie

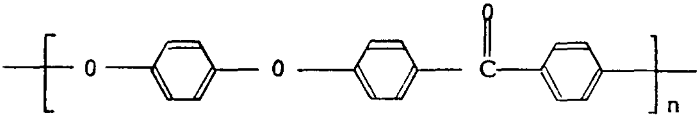
Imperial Chemical Industries PLC, Petrochemicals and Plastics Division, PO Box 90, Wilton, Middlesbrough, Cleveland, TS6 8JE, UK

SUMMARY

Infrared reflection spectroscopy has been used to investigate a series of poly(aryl-ether-ether-ketone) (PEEK) plaques of differing crystallinity. Correlations have been observed between intensity changes in the reflection spectra and the crystallinity as measured by wide angle X-ray scattering (WAXS). These correlations enable estimates to be made of the crystallinity close to the surface and complement the bulk data obtained by WAXS.

INTRODUCTION

Poly(aryl-ether-ether-ketone)(PEEK) is one of a family of commercially available high temperature polymers which are finding increasing use as engineering thermoplastics (1). PEEK is a semicrystalline polymer (2,3) which has the chemical structure:

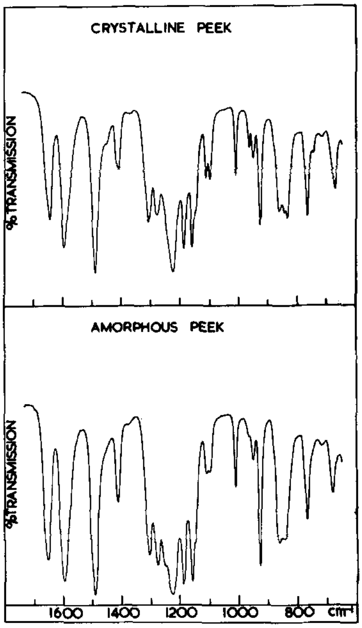


Blundell and Osborn (3) reported recently that PEEK can be considered as a two phase crystalline/amorphous material whose crystallisation behaviour is analogous to poly(ethylene terephthalate) (PET).

In general the mid-IR spectrum of a semicrystalline polymer is affected by changes in crystallinity. However, the observed spectral differences usually arise from the presence of particular conformers in the crystalline regions rather than from the crystalline material itself. Nevertheless it should not be assumed that the mid-IR region cannot provide any information on crystallinity (4). It was the purpose of this study to establish whether correlations could be found between changes in the mid-IR spectrum of PEEK and crystallinity as measured by wide angle X-ray scattering (WAXS).

EXPERIMENTAL

The PEEK samples used in this investigation were the series of plaques prepared by Blundell and Osborn and used in their study of the morphology of PEEK (3). Details of the sample preparation and the subsequent determination of crystallinity by WAXS are discussed in reference 3.



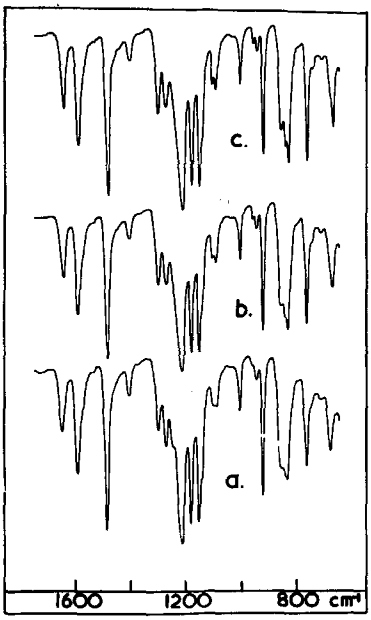


FIGURE 1 Transmission spectra
upper trace - crystalline PEEK
lower trace - amorphous PEEK

FIGURE 2 MIR spectra
(a) amorphous (b) 26%
(c) 40% crystalline

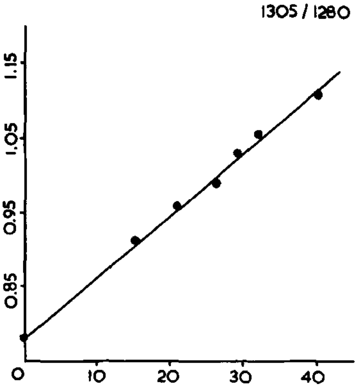


FIGURE 3 ABSORBANCE RATIO VS % CRYSTALLINITY

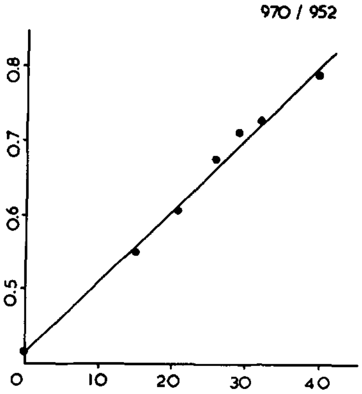


FIGURE 4 ABSORBANCE RATIO VS % CRYSTALLINITY

Infrared spectra of amorphous and crystalline PEEK samples were recorded on a Perkin-Elmer 580B spectrophotometer linked to a model 3600 Data Station. Multiple Internal Reflection (MIR) spectra were obtained using a Wilks model 9 MIR attachment and a thallium bromo-iodide (KRS-5) reflection element with 60^{o} angle of incidence.

RESULTS

In general aromatic polymers such as PEEK are strongly absorbing in the mid IR and prove difficult to compression mould thin enough to observe the more intense absorption bands. The transmission spectrum (1750-650 cm^{-1}) of a thin film of amorphous PEEK ($\sim$10 μm) is shown in figure 1 together with the spectrum of the partially crystalline film produced by compression moulding the amorphous material at 300°C for 10 minutes and cooling slowly to room temperature. Several differences between the spectra of the amorphous and crystalline material are immediately obvious. As expected with increasing crystallinity some bands become both sharper and more intense, presumably as a result of molecular units in the correct conformation crystallising, whilst other bands decrease in intensity.

Since the majority of PEEK samples of commercial interest are unlikely to be in a form suitable for transmission spectroscopy it was of interest to establish whether these differences, as measured by the MIR technique, could be correlated against crystallinity. The series of plaques prepared by Blundell and Osborn (3) were chosen as a suitable set of samples since not only had their crystallinity been determined by WAXS and their homogeneity established by DSC but also their method of preparation reduced possible interference from molecular orientation effects. Figure 2 shows the MIR spectra of samples estimated to be amorphous, 26 and 40% crystalline. Figures 3 and 4 show the correlations obtained between WAXS crystallinity and the MIR absorbance ratios 1305/1280 cm^{-1} and 970/952 cm^{-1}. Band ratios have been used since the intensity of MIR spectra are dependent on the area of contact between the sample and the reflection element.

Unlike WAXS the depth of penetration of the IR radiation is $\sim$1 μm (5) thus figures 3 and 4 indicate that in certain cases it is possible to use MIR spectroscopy as a method of estimating the crystallinity of PEEK within 1-2 μm of the surface. This information complements the bulk data obtained by X-ray techniques.

REFERENCES

1 Attwood T E, Dawson P C, Freeman J L, Hoy L R J, Rose J B and Staniland P A. Polymer 22,1096 (1981)
2 Dawson P C and Blundell D J. Polymer 21,577 (1980)
3 Blundell D J and Osborn B N. Polymer 24,953 (1983)
4 Willis H A and Cudby M E A, in "Structural Studies of Macromolecules by Spectroscopic Methods", ed by K J Ivin, Wiley, London, 81 (1976)
5 Harrick N J, "Internal Reflection Spectroscopy", Interscience New York (1967)

Accepted April 6, 1984