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Effects of pressure on the electronic spectroscopy of poly(*p*-phenylene benzobisoxazole)

M. Anne Leugers* and Steven M. Lefkowitz
Analytical Sciences, The Dow Chemical Company, Midland, MI 48667, USA
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The effect of compression on the fluorescence and Raman spectra of poly(*p*-phenylene benzobisoxazole) (PBO) fibre and a PBO/amorphous nylon blend has been investigated qualitatively at various excitation wavelengths. A substantial red-shift in the fluorescence maxima is observed upon increasing pressure both in PBO fibres as well as in the PBO/amorphous nylon blend. The shift is consistent with that observed for aromatic molecular crystals. This observation strongly suggests that certain features in the fluorescence emission are due to interchain interactions.

(Keywords: fluorescence; PBO; pressure)

Introduction

Poly(*p*-phenylene benzobisoxazole) (PBO) has been shown to be highly fluorescent, with its fluorescence spectra sensitive to the structure of the aggregated chains[1,2]. The origins of the fluorescence emission of PBO are not well understood and this study was undertaken in order to elucidate the role of interchain proximity. A large red-shift ($\sim$3300 cm^{-1}) is observed upon coagulation of PBO from acid solution. In this process the PBO chain is deprotonated, the PBO chains are no longer electrostatically repelled, and strong Van der Waals' interactions between chains are formed[3]. Recent studies have demonstrated that the dominant cause for the red-shifted fluorescence is the subsequent aggregation of the chains following deprotonation[1]. The role of interchain proximity in the fluorescence emission of PBO is not well understood and the qualitative effect of decreasing interchain distance by raising the external pressure on PBO was investigated.

Experimental

PBO/amorphous nylon films (30/70, cast from 0.6% polymer/methanesulfonic acid saturated with methanesulfonic acid anhydride and added sodium methanesulfonate) were prepared as described previously[2]. The 'as-spun' PBO fibre used in this study was produced in the standard manner and was not subjected to heat treatment. The kinkband regions in the PBO fibres examined in this study were generated by placing as-spun fibres between pieces of tape and rapidly pulling them apart in order to cause large ($\sim$2–3 μm wide) bands in the fibres, visible at 50–100 × in the light microscope.

Raman, fluorescence and transmission spectra were measured in a diamond anvil cell (DAC) in the non-hydrostatic mode, and pressures were estimated from frequency shifts of the Raman active band at $\sim$1620 cm^{-1}. The fibres were mounted with the fibre axis parallel to the diamond faces and the pressure exerted across the diameter of the fibre. Raman (and concomitant) fluorescence spectra of PBO fibres and films were measured with excitation at 488 nm provided by a Model 95 Lexel argon ion laser. In addition, the emission at very long wavelengths was excited with the 752.2 nm line of a Lexel RamanIon laser. Absorbance spectra were obtained by measuring the transmission of the PBO/amorphous nylon in the DAC *versus* a 1 mm aperture on a Shimadzu model UV-3101PC spectrophotometer. Pressure estimates were made by measuring the centre of mass of the $\sim$1620 cm^{-1} band and using previously measured Raman shifts of PBO as-spun fibre *versus* applied load in tension. The vibrational band shift *versus* load has been found to be linear to failure both in tension[4] and compression[5], thus the position of the band yielded an estimate of the pressure at the analysis site in the fibre and was not an average across the diamond anvil faces.

The spectrometer employed for these studies was a Dilor model XY triple spectrometer with 1200 l mm^{-1} gratings operating in the subtractive double mode. The detector was a liquid-cooled Thompson silicon charge-coupled detector, providing good sensitivity with excitation at long wavelengths.

Results and discussion

The effect of external pressure on the fluorescence spectrum of PBO as-spun fibres is shown in *Figure 1a* for excitation at 488 nm. A strongly overlapped doublet with maxima at $\sim$18 180 and $\sim$17 100 cm^{-1} is observed at the lowest pressure of $\sim$12 kbar (1 bar = 10^5 Pa). Upon further compression, the peaks coalesce into a broadened singlet with the high energy edge shifted slightly. At the highest pressure, estimated to be $\sim$34 kbar from previous measurements of shift *versus* applied load, the maximum is observed at 16 260 cm^{-1} (615 nm), a total shift of $\sim$2000 cm^{-1} from the original peak. Over this range, the 1620 cm^{-1} vibrational mode shifted from $\sim$1620 to 1632 cm^{-1} ($\sim$12 cm^{-1} or $\sim$0.35 cm^{-1} kbar^{-1}). This shift is in the typical range for internal modes of organic molecules[6]. In all measurements, the effect was found to

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* To whom correspondence should be addressed

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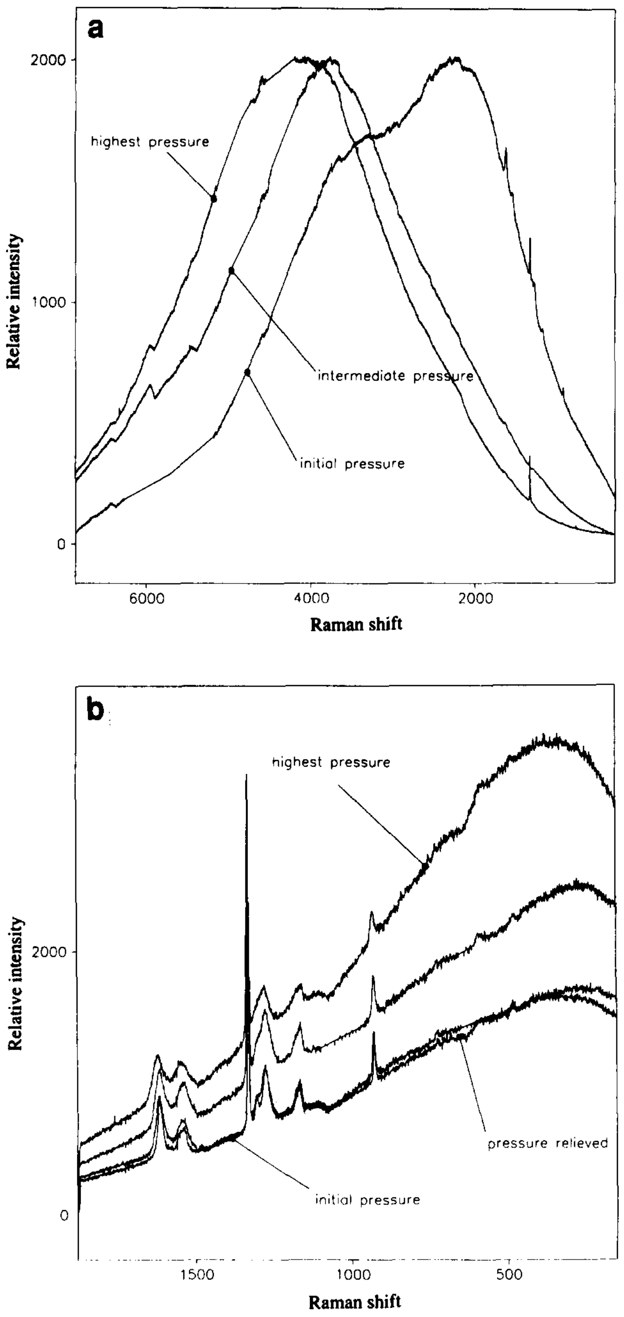

Figure 1 Normalized fluorescence emission spectra of PBO as-spun fibres in DAC at various pressures: (a) excitation at 488 nm; (b) excitation at 752 nm

be reversible as the fluorescence spectrum returned to the original curve or was slightly blue-shifted from the original upon pressure release.

Evidence of a red-shifted electronic transition is also observed by exciting directly into the 'tail' of the long wavelength component at 752 nm with the krypton ion laser. The effect of increasing the compression on the as-spun PBO fibres is shown in *Figure 1b*. At the lowest pressure in the DAC the fluorescence intensity maximum is approximately half that observed at the highest pressure in this set of experiments (~ 17 kbar). Again, the effect of pressure is to increase the fluorescence intensity at long wavelengths.

The observed red-shift in electronic transitions with compression to high pressures has been thoroughly documented for molecular crystals[6–8] and results from the enhanced excitation delocalization between molecules as the intermolecular spacing decreases[9]. The results observed here for PBO fibres are quite consistent with this model.

These results strongly indicate that the fluorescence maxima at 550 and 585 nm are due to states arising from interchain interactions. The 500 nm emission maximum which is observed with excitation at wavelengths of <450 nm is absent in these spectra, presumably because of the longer wavelength of excitation used in the studies[1]. All of these maxima (500, 550, 585 nm) observed in PBO solids, however, have been ascribed[1] to states arising from the aggregated PBO structure, as the neutral unaggregated PBO rod exhibits its 0–0 fluorescence band at ~ 430 nm.

Some authors[10] have observed similar red-shifts in the absorption band edge in an aromatic polyimide film at

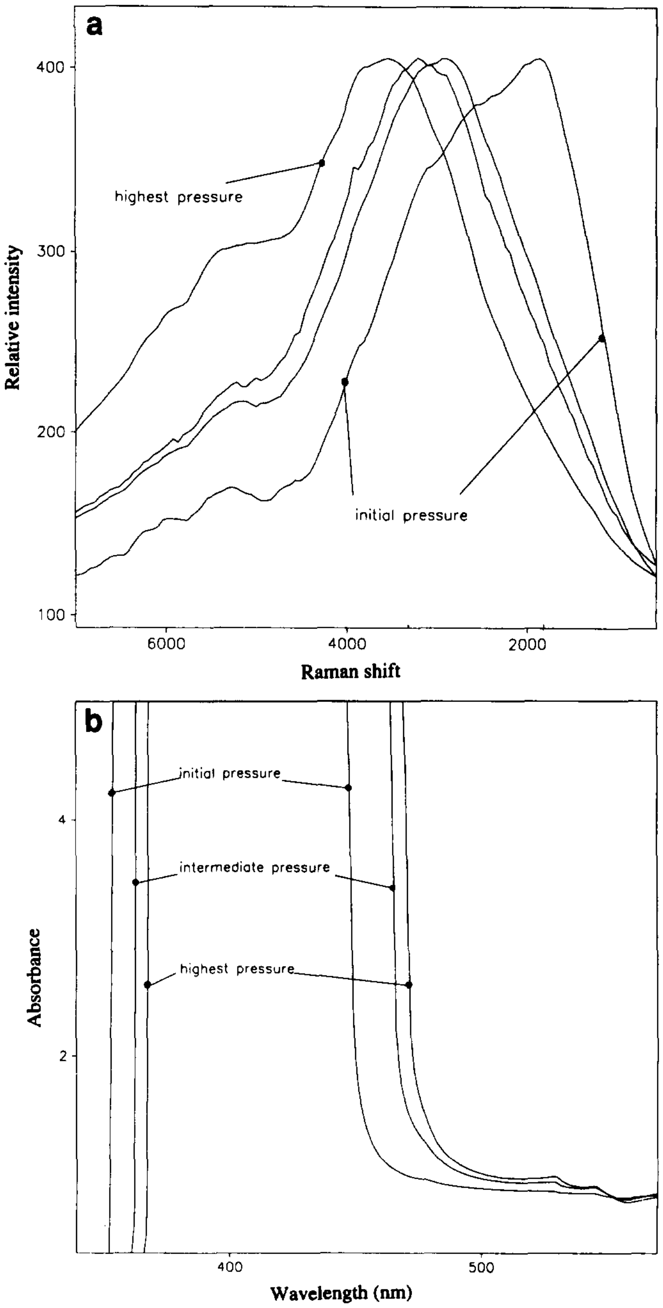

Figure 2 Electronic spectra of PBO/amorphous nylon films at various pressures in DAC: (a) fluorescence emission spectra excited at 488 nm; (b) absorption 'spectra' of a 1% PBO/nylon film *versus* pressure

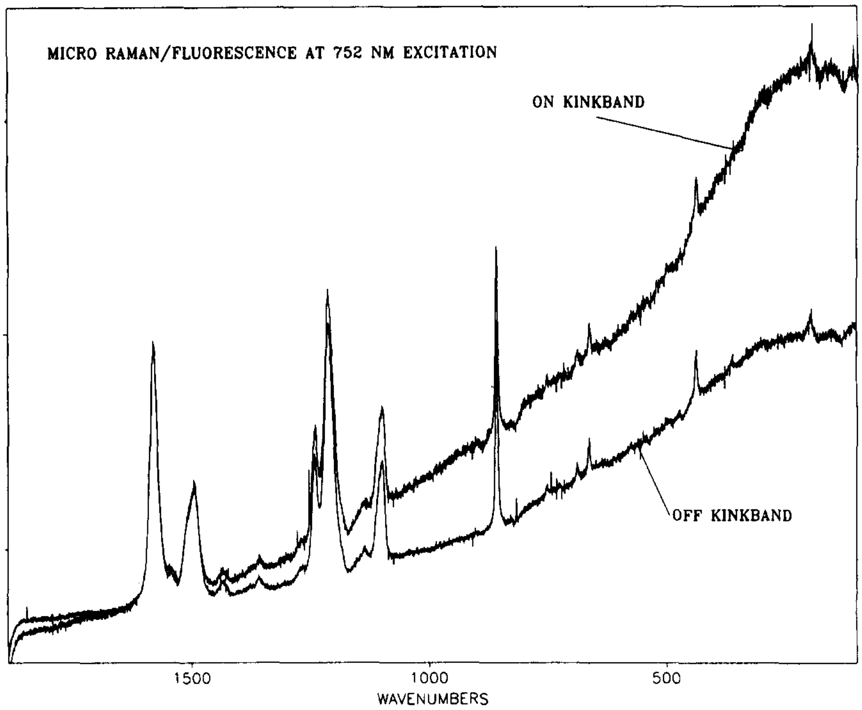

Figure 3 Raman spectra of $\sim 1\,\mu m^2$ area on and adjacent to kinkband in PBO fibre. The spectra have been normalized to the intensity of the $1620\,cm^{-1}$ band

elevated pressure and suggested the possibility that the origin of the shift is due to the perturbation of a charge transfer species between the imide and diphenyl ether portions of the polymer backbone. Although we cannot rule out this possibility as the origin of the red-shift in PBO, it is not obvious to us which moieties in the PBO molecule could give rise to a strong ground state charge transfer complex.

The fluorescence of PBO/amorphous nylon film blends was also investigated at high pressures. The results, shown in *Figure 2a,* are qualitatively the same as that for the PBO as-spun fibres, a red-shift in the fluorescence emission with higher pressure which is reversible upon the release of the pressure. Although the sample was not sufficiently thin to allow the measurement of a transmission spectrum, the blue and red edges of the optical absorption were measured with increasing pressure and the results are shown in *Figure 2b.*

The transmission results of the PBO/amorphous nylon measurements indicate that the observed red-shift on compression is clearly a bulk property and not due to compression of defect sites or traps in the material. Again, the red-shifted transmission spectra were found to be reversible upon release of pressure. Excitation on and immediately adjacent to the kinkbands in the damaged PBO fibres with the 752.5 nm laser line yielded the results typified by the spectra in *Figure 3.* At 10 different sites in the damaged PBO fibre, spectra exhibited similar results; the higher fluorescence was always obtained on the kinkband rather than immediately adjacent to it.

Kinkbands, which result from fibre damage, are believed to be regions of compression in the fibre[11]; the enhanced fluorescence intensity observed in these experiments in the region of the kinkband could support this supposition. However, the specific microscopic mechanisms responsible for the enhanced fluorescence in the kinkbands are not clear to us at this time and require further study.

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