An *in situ* Raman study of the electrochemical doping of oriented Durham polyacetylene

J. Barker and K. P. J. Williams
British Petroleum Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, UK
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The results of a Raman study on electrochemically Na^+ doped oriented Durham polyacetylene are presented. The spectral changes observed suggest that low doping levels cause an effective shortening of the conjugated length. Doping to 3 mol% Na^+ gives a two-phase behaviour for the doped polymer. Beyond 6 mol% the spectra recorded are consistent with a delocalized structure. An additional Raman band at 1268 cm^{-1} is assigned to a carbon–carbon stretching mode which has significant double-bond character. Following an electrochemical doping–undoping cycle the polymer does not return to the pristine state but shows signs of either polymer degradation or residual dopant ion remaining in the material.

(Keywords: polyacetylene; doping; Raman spectroscopy)

INTRODUCTION

The doping of conducting polymers such as polyacetylene causes electronic, optical, magnetic and structural changes to occur in the material[1–3]. Chemical doping is carried out by exposure of the polyacetylene to electron-withdrawing compounds such as AsF_5 and SbF_5 to oxidize the polyacetylene and produce p-type doped material, or by exposure to electron-donating compounds such as n-butyl lithium and sodium naphthilide to reduce the polyacetylene and produce n-type doped samples. Chemical doping methods, however, lead to doping ion inhomogeneity within the sample and for this reason electrochemical techniques are normally preferred.

Electrochemical doping allows both improved dopant ion homogeneity and effective dopant ion concentration fine control. This control has been exploited by various *in situ* experiments to gain considerable insight into the subtle electronic and structural changes occurring in the polyacetylene during the doping process[4–6].

Resonance Raman spectroscopy is a well-established technique for obtaining important structural information from polyacetylene[7–11]. The major features for undoped material are two intense bands centred around 1100 cm^{-1} and 1500 cm^{-1} which can be assigned to the ν_1 and ν_2 modes and correspond mainly to the C–C and C=C vibrations respectively. Dispersion of these band positions is observed when laser excitation at differing wavelengths is employed. The dispersion of the ν_2 band has been attributed to either a variation of the conjugated chain length[12] or the amplitude modes of the Peierls distortion[13].

The Raman spectrum of p-type doped Shirakawa polyacetylene is relatively featureless[14] and normally characterized by a single broad band around 1600 cm^{-1}. In contrast, the Raman data collected from n-type doped polyacetylene samples show distinct spectral changes with the appearance of new, relatively intense bands, together with a shift in the original bands arising from the undoped material[15–18]. The Raman spectra of Li^+ doped Shirakawa polyacetylene show a new and intense feature around 1275 cm^{-1}, together with bands around 1140 and 1580 cm^{-1}. The exact position of these bands has been shown to depend heavily on the laser excitation wavelength used[15]. The interpretation of these data, especially the feature around 1275 cm^{-1}, remains controversial.

Raman spectra for Na^+, K^+ and Rb^+ doped polyacetylene show essentially the same spectral features as Li^+ doped samples[16]. Overall, the recorded spectra indicate a gradual movement of the Raman bands to lower wavenumber with increasing dopant ion size[19]. Small variations in the positions of these bands are also observed as a function of dopant ion concentration.

The data presented in this paper are the results of a detailed *in situ* Raman study during electrochemical Na^+ doping of well-oriented Durham route polyacetylene. The results of the pristine, undoped and the electrochemically cycled oriented material are also presented.

This is the first *in situ* electrochemical doping/Raman study on oriented samples of Durham polyacetylene. The data presented are discussed in terms of the structural information that may be inferred from the Raman spectra. The results are also compared with those reported for chemically and electrochemically doped Shirakawa polyacetylene samples.

EXPERIMENTAL

The oriented Durham polyacetylene used in this study had an approximate draw ratio of 8:1. The material was annealed for 20 h at 80°C under vacuum to ensure conversion to the *trans* isomer. The precise method for preparation and orientation of the films has been discussed in detail elsewhere[19–21].

The Raman/electrochemical cell design is shown schematically in *Figure 1*. The cell consisted of a sodium electrode pressed on to a nickel mesh current collector and the oriented polyacetylene film mechanically pressed on to a platinum gauze. These electrodes were separated

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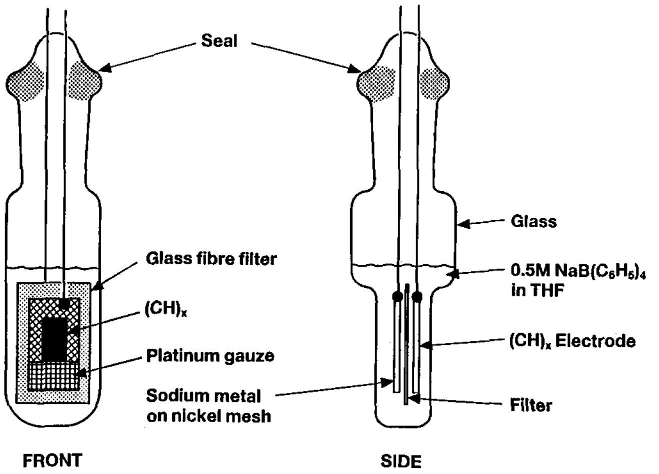

Figure 1 Electrochemical cell design for *in situ* Raman experiments

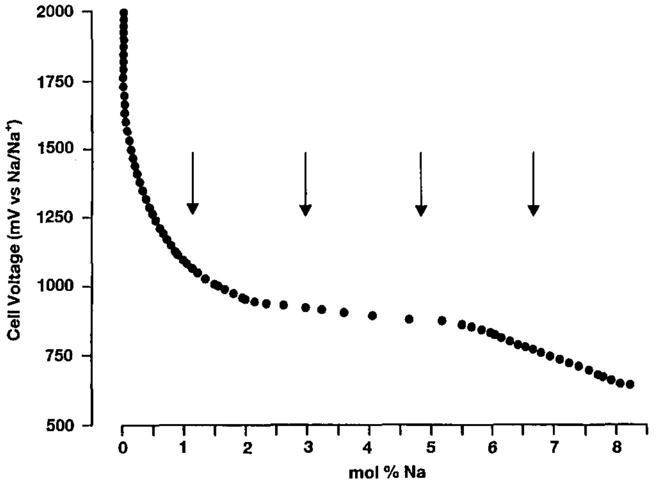

Figure 2 Electrochemical voltage spectroscopy of electrochemical cell

by a pre-dried glass fibre filter paper. The electrolyte used was carefully purified 0.5 M $NaB(C_6H_5)_4$ in tetrahydrofuran. The cell design ensured that the electrode separation and electrolyte volume were kept to a minimum. This latter condition is particularly important in order to minimize the cell side-reactions arising from interactions between electrolyte impurities and the reactive Na^+ doped polyacetylene film. Such reactions cause cell instability and poor doping reaction reversibility.

An electrochemical cell, prepared under identical experimental conditions and using a piece of the same polyacetylene film, was characterized by electrochemical voltage spectroscopy. This technique has been used extensively by our group to investigate the electrochemical properties of Durham polyacetylene[22–24]. *Figure 2* shows the cell voltage (*versus* Na/Na^+) as a function of dopant ion concentration (mol% Na^+) derived from one cycle of the cell. This 'calibration curve' was used during the Raman investigation to establish the precise dopant ion concentration of the polyacetylene.

Raman data were obtained from an Anaspec 33 laser Raman spectrometer interfaced to an Apricot microcomputer system for data acquisition. The spectra were recorded with the polyacetylene aligned such that the direction of stress of the film was parallel to the *E* vector of the laser. The lasers used to excite Raman spectra were a Spectra Physics model 164 Kr^+ laser and a Spectra Physics model 165 Ar^+ laser. These provided the red (647.1 nm) and blue (457.9 nm) excitation respectively.

RESULTS AND DISCUSSION

Figures 3a and *b* show the resonance Raman spectra recorded for the pristine polyacetylene film with red (647.1 nm) and blue (457.9 nm) laser excitation respectively. ν_1 and ν_2 wavenumber positions have been measured at 1071 cm^{-1} and 1460 cm^{-1} for red laser excitation, and 1114 cm^{-1} and 1496 cm^{-1} recorded using blue laser excitation. These values are slightly different to previously recorded data from pristine oriented material indicating a slightly inferior film which showed only a weak bimodal character.

Figure 4 shows the changes seen in the Raman spectra as a function of Na^+ concentration using red excitation.

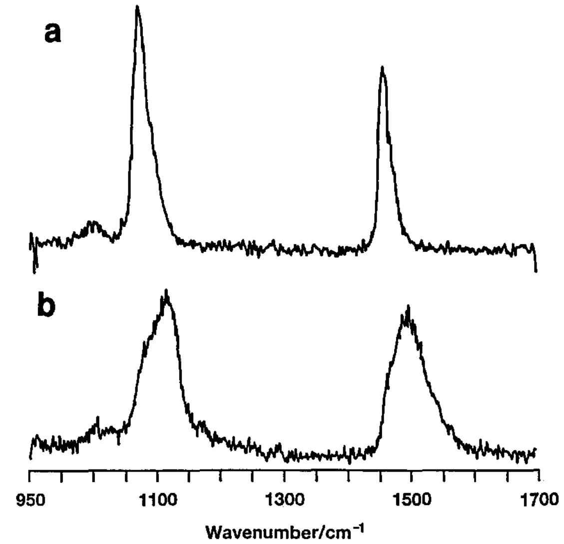

Figure 3 Resonance Raman spectrum of pristine oriented Durham polyacetylene at (a) $\lambda_e = 647.1$ cm and (b) $\lambda_e = 457.9$ nm

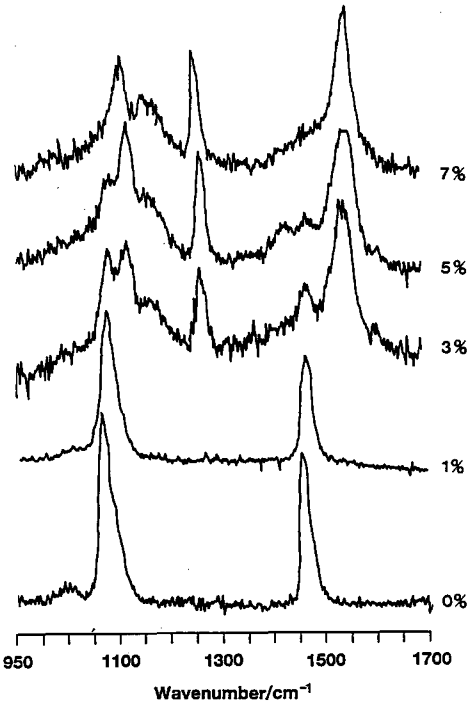

Figure 4 Raman spectra from Na^+ doped oriented polyacetylene at different levels. $\lambda_e = 647.1$ nm

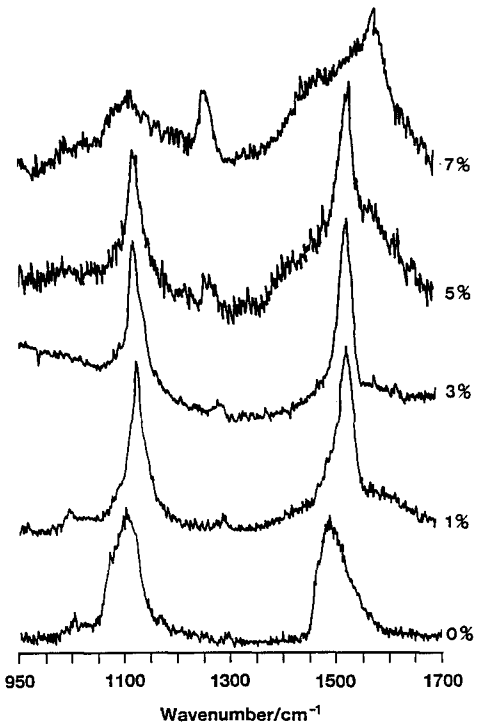

Figure 5 Raman spectra from Na$^+$ doped oriented polyacetylene at different levels. $\lambda_e = 457.9$ nm

Table 1 Raman wavenumber shifts (cm^{-1})^a recorded from doped oriented Durham polyacetylene using red and blue laser excitation

	Laser exciting line	
Na$^+$ (mol%)	647.1 nm	457.9 nm
Pristine	1460, 1071	1496, (1468sh), 1291 1114, (1078sh)
1	1468, 1077	1532, (1496sh) 1291, 1132
3	1546, 1468, 1265 (1170sh), 1125, 1080	1534, 1289, 1128
5	1552, (1470sh), 1268 (1168sh), 1128, (1090sh)	(1577sh), 1534 1272, 1130
7	1563, 1262 (1170sh), 1125	1584, (1490sh) 1268, 1125
Undoped	1462, 1075	1530, (1496sh) 1291, 1130

^{a} Shifts quoted ±1 cm^{-1}

Figure 5 shows a similar plot using blue laser excitation. *Table 1* summarizes the Raman wavenumber data, showing numerically the shift in position of the ν_1 and ν_2 bands during doping, together with details of new Raman features.

At low doping levels (1 mol%) the sample shows some spectral changes compared to the pristine material, particularly using the blue excitation. The ν_2 band using red excitation has shifted from 1460 cm^{-1} to 1468 cm^{-1} and lost a good deal of its original asymmetry.

For the blue excitation the ν_2 band has moved 36 cm^{-1} to 1532 cm^{-1}, although there remains a distinct shoulder at around 1496 cm^{-1}, i.e. the position recorded for the pristine material. These shifts in band position and change in band shape at low doping levels are fully consistent with an effective shortening of the overall conjugated polyene sequence length. Similar results have been obtained previously from Shirakawa polyacetylene samples[18,25].

At doping concentrations of 3 mol% and above, very dramatic spectral changes are observed using red excitation, with Raman features prominent at 1125, 1170, 1165 and 1546 cm^{-1}. In addition, the intensity of the ν_1 and ν_2 bands positioned at 1080 and 1468 cm^{-1} are very much weaker. The assignment of the extra Raman bands is not straightforward. It has been suggested from similar studies on Shirakawa polyacetylene that the extra bands can be interpreted in terms of a shortening/lengthening of the polyene sequence length[18,25]. If one were to assign the bands observed at 1125 and 1546 cm^{-1} to very short *trans* (C=C) sequence lengths, then a much shorter sequence length (and hence higher ν_1 and ν_2 values) would be probed using the blue excitation. However, values of 1128 and 1534 cm^{-1} for ν_1 and ν_2 using the blue excitation clearly indicate that this is not the case. Therefore it is proposed that the spectra observed here, using 647.1 nm from polyacetylene samples with a dopant concentration greater than 3 mol% Na$^+$, should not be treated in terms of shifts in ν_1 and ν_2 but as a completely separate system. In contrast the spectra recorded using 457.9 nm excitation are reasonably discussed in terms of their ν_1 and ν_2 positional shifts even up to around 6 mol% Na$^+$.

The precise nature of the Raman bands observed with 647.1 nm at doping concentrations greater than 3 mol% Na$^+$ is unclear. The exact position of the high wavenumber band is clearly dependent on the doping concentration. The highest value recorded in this work was for the 7 mol% doped sample at 1563 cm^{-1}. This band movement has also been reported for Shirakawa polyacetylene doped with other n-type doping ions[15].

It has been suggested that the feature observed at 1560 cm^{-1} can be attributed to the presence of short polyene sequences. However, an alternative explanation has been suggested by Zannoni and Zerbi[26] who have established a dynamic model for polyacetylene and then considered the introduction of defects of different symmetry types. The C_{2v} symmetry defect can produce a density of states around 1600 cm^{-1}. This type of defect would correspond to a system where the dopant ions were present in a layered structure (intercalation model) formed by the host polyacetylene chains[27]. However, *in situ* X-ray studies carried out during electrochemical Na$^+$ doping of oriented Durham polyacetylene material are not consistent with the intercalation model for the n-type doping process[5,6].

A new Raman band at 1268 cm^{-1} is also observed at concentrations above 3 mol% with 647.1 nm laser excitation. This peak is less evident with excitation at 457.9 nm and only becomes prominent above 5 mol% Na$^+$. A new and relatively intense Raman band at a similar wavenumber position has also been reported during n-type doping in Shirakawa polyacetylene[17,28]. Several theories have been postulated over recent years.

It has been suggested that this additional peak is equivalent to the weak 1291 cm^{-1} band observed in the Raman spectra recorded from pristine polyacetylene and increases in intensity during doping due to induced disorder, which leads to the formation of short *trans* polyene sequences[29]. Others have studied *FT*i.r. data from doped polyacetylene and have identified three intense doping-induced bands at 1385, 1295 and 832 cm^{-1}. These bands have been assigned to Raman active A_g modes in the i.r. spectrum. The band at 1295 cm^{-1} is then considered to arise from vibronic activation of a

Raman active A_g mode in the i.r. spectrum[30]. Alternatively, calculations by Zannoni and Zerbi[31] have shown that a mode in the range 1250–1300 cm^{-1} is predicted for an undimerized chain (i.e. a totally delocalized system).

From symmetry considerations it was predicted that for an undistorted doped polymer chain a single Raman active mode at 1223 cm^{-1} should exist. A more complete analysis, in which the dynamics of the hydrogen atoms were included, predicted a Raman mode at 1268 cm^{-1}.

More recently, workers have followed a perturbed Green's function method[32,33]. This was originally proposed to explain the properties of doping-induced bands in the i.r. spectrum[34], to account for the new vibrational features seen in the Raman spectrum from n-type doped polyacetylene. The model takes into account the perturbation induced by the trapped charges on the lattice dynamics of the conjugated segments through a parameter Λ which represents a change of the force constant with respect to the unperturbed lattice of the polymeric chain.

The calculations of both Zerbi and co-workers and the Green's function approach provide a good theoretical basis for the interpretation of the extra doping-induced Raman features, seen both from our work on oriented Durham polyacetylene, and from results reported for Shirakawa type polyacetylene. Both models suggest that the principal extra band observed at 1268 cm^{-1} is associated with a carbon–carbon stretching vibration with some double bond character.

Undoping of the polyacetylene film was carried out potentiostatically over a period of around 14 days. The spectra using red and blue excitation, after this undoping stage, are shown in *Figures 6a* and *b* respectively. The charge remaining within the film after the undoping, estimated electrochemically from the open cell voltage, indicated a residual Na$^+$ content of around 0.25 mol%. Further removal of the dopant ion becomes increasingly difficult since decreasing the dopant concentration also causes a concurrent loss in electronic conductivity within the polyacetylene sample.

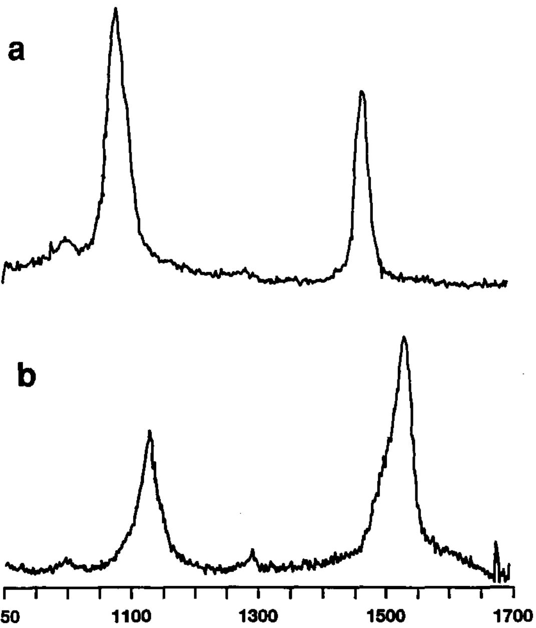

Figure 6 Raman spectrum from undoped oriented polyacetylene at (a) $\lambda_e = 647.1$ nm and (b) $\lambda_e = 457.9$ nm

The residual Na$^+$ content appears to affect the Raman spectra for the undoped sample. The effect was particularly noticeable using the blue excitation. However, there still exists a high concentration of long polyene sequences in the undoped sample since some of the asymmetry returns to the band at 1462 cm^{-1}, seen with the red laser excitation in *Figure 6a*.

It is unclear whether any polymer degradation has occurred during the electrochemical cycling of the sample since it is difficult to differentiate between possible effects due to degradation and those resulting from the small amount of residual Na$^+$ remaining in the sample. Even trace amounts of Na$^+$ will play a significant part in determining the ν_2 band position.

CONCLUSIONS

This resonant Raman investigation of electrochemical Na$^+$ doping in oriented Durham polyacetylene has generated some important results.

Low level doping (1 mol% Na$^+$) leads to an effective shortening of the conjugated *trans* sequences. When these particular polyacetylene samples are doped to around 3 mol% new red-excited Raman features arising from the doped component of the polymer are observed. The bands arising from the blue excitation are thought to correspond to the undoped polymer.

Raman spectra recorded for red and blue excitation from 7 mol% Na$^+$ polyacetylene are both considered to arise from the doped polyacetylene phase.

The doping-induced Raman band at 1268 cm^{-1} seen with both red and blue excitation can be tentatively assigned to a carbon–carbon stretching vibration which is perturbed by the dopant ion yet still retains some double bond character.

Electrochemical undoping does not return the polyacetylene to the pristine state. This condition may be due to either polymer degradation or to the residual Na$^+$ remaining in the sample.

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