A Fourier transform–Raman spectroscopic study of electrically conducting polypyrrole films

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The chemical structure of electrically conducting polypyrrole films has been studied for the first time by Fourier transform (*FT*)-Raman spectroscopy. The technique offers considerable signal-to-noise advantages over dispersive Raman spectroscopy and is useful for the analysis of weak scatterers including conducting polymers. Spectra of polypyrrole doped with *p*-toluene sulfonate and dodecyl sulfate are presented together with spectra obtained from the corresponding dedoped polymers. Samples were analysed in sealed glass containers and spectra obtained in 25 min. Analysis of the *FT*-Raman spectra shows them to be consistent with polaron and bipolaron descriptions of the electron transport mechanism in polypyrrole.

(Keywords: Raman spectroscopy; Fourier transform; polypyrrole; conducting polymer; electron transport)

INTRODUCTION

Polypyrrole is a highly conductive polymer that can be readily prepared electrochemically and by solution polymerization. Its stability in air makes it a possible prototype material for a diverse range of applications, which include lightweight batteries, electromagnetic shielding materials and chemical sensors.

The electrical conductivity and physical properties of polypyrrole, including stability, are very dependent upon synthesis conditions and the choice of dopant. However, the chemical structure of polypyrrole, the nature of the polymer–dopant interaction and the molecular structure of defects such as polarons are still not well understood[1].

Raman spectroscopy[2–7] has been used to characterize polypyrrole films, but the broad absorption bands and rough sample surfaces give weak Raman spectra[4]. The bands are resonance enhanced at visible laser wavelengths, as the oxidized polymer absorbs strongly in this region[3,6], but the laser source must be defocused and operated at low powers to avoid sample degradation, with a consequent reduction in Raman scattering intensity. This, together with the fluorescence observed from some films, restricts the usefulness of the dispersive technique. Fourier transform (*FT*)-Raman spectroscopy, however, is a new technique that is well placed for the analysis of weak scatterers. Signal-to-noise ratios are enhanced by the multiplex and throughput advantages associated with interferometer-based spectrometers, and the near-infra-red (n.i.r.) laser source minimizes interference from sample fluorescence.

In this paper we present *FT*-Raman spectra obtained from electrochemically prepared polypyrrole films doped with *p*-toluene sulfonate (pTS) and dodecyl sulfate (DDS). These spectra are compared with those from the corresponding reduced polymers after dedoping and shed light on the chemical changes that facilitate electron transport on doping.

EXPERIMENTAL

Polypyrrole films were grown electrochemically in an aqueous electrolyte solution containing 0.1 M freshly distilled pyrrole and 0.1 M sodium DDS or sodium pTS dopant under a nitrogen blanket. DDS-doped films were grown at a constant current density of $2\,\mathrm{mA\,cm^{-2}}$ for 120 min and pTS-doped films at $5\,\mathrm{mA\,cm^{-2}}$ for 2 min and $3\,\mathrm{mA\,cm^{-2}}$ for 120 min. Dedoping was achieved by reversing the polarity of the electrodes. The films were easily removed from the electrode and washed with a mixture of water and acetonitrile to remove any excess dopant. Samples were stored under vacuum prior to spectroscopic analysis.

FT-Raman spectra were obtained at $8\,\mathrm{cm^{-1}}$ resolution using a Bruker IFS 66 spectrometer with an FRA 106 Raman module employing a special Ge detector, a Si/CaF_2 beam-splitter and a defocused, diode-pumped, Nd:YAG laser operating at $1.06\,\mu m$ and 50 mW power. Samples were presented to the spectrometer in glass ampoules.

RESULTS AND DISCUSSION

pTS polypyrrole

Figure 1 shows the *FT*-Raman spectra of pTS polypyrrole in both the fully doped and dedoped states. The laser referencing of the interferometer mirror position provides excellent wavenumber stability compared to dispersive instruments, which have to be calibrated

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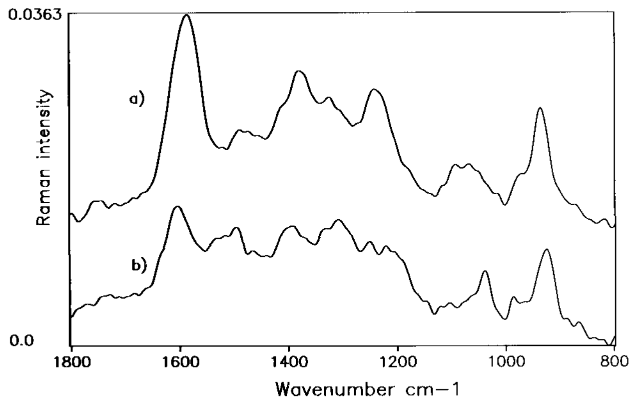

Figure 1 *FT*-Raman spectra of (a) doped and (b) dedoped pTS polypyrrole

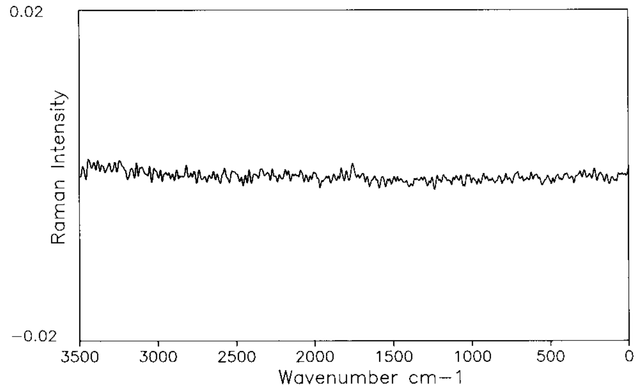

Figure 2 Difference spectrum of pTS polypyrrole subtracted from the spectrum of the same material 24 h later

frequently. This is amplified by *Figure 2*, which shows the difference spectrum of pTS polypyrrole subtracted from a spectrum of the same material 24 h later. The difference spectrum also indicates that there has been no sample degradation by the laser during the measurement.

The fully doped spectrum is resonance enhanced since the oxidized polymer absorbs at the source wavelength of 1.06 μm[6,8]. The broad bandshapes suggest a disordered structure with short conjugation sequences[4]. On dedoping, the electrical conductivity is reduced by 10- to 20-fold, but chemical analysis revealed[9] that the dedoped polymer still contained a significant amount of dopant and, therefore, was probably not totally reduced. It is thought that the dedoping process for large anions like pTS and DDS is sterically controlled and that these anions are difficult to remove from the thick films ($\approx 100\,\mu$m) prepared for this study. Consequently, *FT*-Raman bands arising from the unreduced portion of the dedoped polymer will also be enhanced.

These resonance-enhanced bands give a valuable insight into the molecular structure of species responsible for the associated electronic transition at the excitation wavelength. Scott *et al.*[10] and Brédas *et al.*[11] have assigned the visible and n.i.r. absorption bands to the dication at high doping levels and to the radical cation at low doping levels. Furukawa *et al.*[3] have assigned the n.i.r. electronic band to the dication, which on reduction yields radical cations that are in turn further reduced to the neutral polymer. The latter two species were considered to account for absorptions in the visible spectrum.

Dispersive Raman spectra of doped polypyrroles have provided evidence for the existence of polarons (radical cations) and bipolarons (dications)[3,7], which act as charge carriers. The radical cation and dication may be considered to be localized structural defects associated with the conjugated carbon backbone. The radical cation arises from the pair formation of a positive hole and a dopant anion[6]. This results in a deviation from the sp^2 hybridized structure of the neutral polypyrrole backbone, as it is deficient of π-electrons. A concomitant change in Raman shifts is therefore observed on reduction as the polymer relaxes back to its neutral form[3]. The dication will also give rise to structural changes and these will be considered in more detail below.

From isotopic substitution studies, Furukawa *et al.*[3] have assigned the resonance Raman bands (632.8 nm excitation) of ClO_4^--doped polypyrrole at 1369, 1229, 1082 and 931 cm^{-1} to antisymmetrical C–N stretching, antisymmetrical C–H in-plane bending, symmetrical C–H in-plane bending and ring deformation associated with the dication, respectively. The C=C stretching peak at 1580 cm^{-1} was assigned to an overlap of bands arising from the radical cation and dication. Other bands at 970 and 1060 cm^{-1} were reported to be characteristic of radical cations and were assigned to ring deformation and symmetrical in-plane C–H bending, respectively.

Similar bands associated with the radical cation and dication are present in the *FT*-Raman spectrum of fully doped pTS polypyrrole shown in *Figure 1*. On dedoping, the spectrum reveals a significant decrease in the intensity of the 1585 cm^{-1} dication and radical cation peak relative to the 1488 cm^{-1} skeletal band. This is consistent with a reduction in the concentration of dications and possibly radical cations on dedoping. Further evidence for the presence of these species in the oxidized polymer comes from the symmetrical in-plane C–H bending bands at 1091 and 1066 cm^{-1}, which also decrease in intensity on dedoping. The dication band at 935 cm^{-1} is still prominent after dedoping, indicating that the polymer has not been fully reduced, as was confirmed by elemental analysis[9]. However, the band is broader and shifted to 925 cm^{-1}, which suggests the formation of one or more new polymer species. Further evidence for this conclusion is given below.

Umapathy and Hester[7] have used resonance Raman spectroscopy to provide evidence for the existence of bipolarons in ClO_4^--doped polypyrrole on colloidal TiO_2. They have shown that both aromatic (*Figure 3a*) and quinonoid-type structures (*Figure 3b*) linked by either α–α or α–β carbons are present in solution-polymerized polypyrrole. The latter structure is considered to be the structural basis of the bipolaron (*Figure 3c*) as its doped form is thermodynamically more favourable than the aromatic form owing to its low ionization potential and electron affinity[12]. Both structures give rise to bands with distinct Raman shifts and may be used to identify oxidized and neutral groups within the polymer.

The ultra-violet/visible (u.v./vis.) spectrum of polypyrrole on TiO_2 is, however, very different from that of the electrochemically grown polypyrroles studied here. It exhibits only one broad absorption at 460 nm that is attributed to the transition between the valence band and the second bipolaron level (hw_2)[7]. As stated earlier, corresponding transitions in electrochemically grown polypyrroles appear in the n.i.r.[3]. Consequently, the resonance *FT*-Raman spectra of the electrochemically

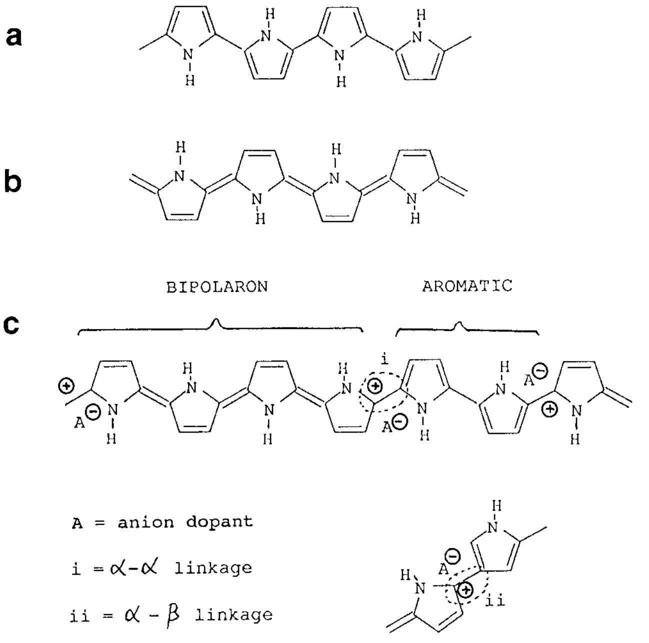

Figure 3 (a) Aromatic polypyrrole, (b) quinonoid polypyrrole and (c) proposed disordered polypyrrole structure[7]

Figure 4 *FT*–Raman spectra of (a) doped and (b) dedoped DDS polypyrrole

prepared polypyrroles obtained with a 1.06 μm source should also show evidence of the quinonoid bipolaron structure. This was confirmed by the presence of a strong quinonoid band at 1091 cm^{-1} in fully doped pTS polypyrrole. It decreases in intensity on dedoping and a new band appears at 1039 cm^{-1}, which is assigned to an aromatic C–H in-plane deformation mode characteristic of the neutral polymer. The spectrum of the reduced polymer also provides supporting evidence for the increased concentration of neutral aromatic polymer segments since the broad C=C stretching band at 1585 cm^{-1} has shifted to 1602 cm^{-1} and is more antisymmetric on the high-wavenumber side with a distinct shoulder at 1630 cm^{-1}.

Virdee and Hester[5] have reported that there is some resemblance between the resonance Raman spectra of polypyrrole and polyacetylene, since both conducting polymers have an extended conjugated π-electron system. They have tentatively suggested that, as the spectra of the two polymers were similar, polypyrrole may have *trans* and *cis* segments like polyacetylene. Within the pyrrole rings, the conjugated carbon double bonds are intrinsically of *cis* geometry, but there are opportunities for both *cis* and *trans* geometries for adjacent rings. The *FT*–Raman spectra of pTS polypyrrole reported here tend to confirm this conclusion. On dedoping, a new broad C=C stretching doublet is observed at 1520 and 1540 cm^{-1}, which is possible evidence for the *cis* geometry of neighbouring pyrrole units in the neutral polymer. This conclusion is supported by the presence of another new band at 1251 cm^{-1}, which together with the band at 925 cm^{-1} are comparable with those found in *cis*-polyacetylene[13].

DDS polypyrrole

The resonance *FT*–Raman spectrum of fully doped DDS polypyrrole shown in *Figure 4* is broadly similar to that of the pTS spectrum. This confirms that both *FT*–Raman spectra are dominated by polymer vibrations, and accordingly the bands between 900 and 1600 cm^{-1} in the DDS spectrum may be assigned to the same skeletal motions as for the pTS-doped polymer.

Despite this broad similarity, there are some spectral differences, which may relate to differences in their relative conduction mechanisms. The quinonoid dication band at 1091 cm^{-1} is extremely weak in the DDS spectrum and only the radical cation band at 1064 cm^{-1} is evident. Further, on dedoping there is no reduction in intensity of the 1577 cm^{-1} band. The 929 cm^{-1} dication peak is also weaker and closer in intensity to the 970 cm^{-1} radical cation band. From these observations it is tentatively suggested that the concentration of dications is less in DDS- than in pTS-doped polypyrrole and that the radical cation assumes a more prominent role in electron transport in the former. This conclusion is consistent with the lower conductivity recorded for the DDS-doped polymer (4 S cm^{-1}) compared to its pTS analogue (25 S cm^{-1}).

Comparison of the *FT*–Raman spectra with those obtained by *FT*i.r. spectroscopy will be addressed in a further publication.

CONCLUSIONS

FT–Raman spectroscopy has been shown to be a valuable technique for the structural analysis of polypyrroles. The signal-to-noise advantage available from the *FT*–Raman technique compared to conventional dispersive (with photomultiplier detection systems) Raman instruments allows spectra to be obtained in 25 min with minimum sample preparation. Results obtained from *ex situ* samples show the potential of this technique for the *in situ* analysis of polymer growth on electrodes, for example, where high sensitivity is required to follow subtle structural changes. In this regard, recent developments in charge coupled devices (CCDs) may offer increased speed and sensitivity at the expense of greater fluorescence[14,15] but such instruments are not yet commercially available.

The *FT*–Raman spectra of pTS- and DDS-doped polypyrroles obtained at 1.06 μm are resonance enhanced, and bands result from radical cation (polaron) and dication (bipolaron) groups responsible for electronic transitions at this wavelength. The spectra of the pTS polymer provide evidence for both species but the DDS spectra predominantly show the presence of radical cations. It is tentatively concluded that electron transport in pTS-doped polypyrrole is facilitated by both radical cations and dications, whilst the conduction mechanism in DDS-doped polypyrrole is essentially by radical cations.

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