Raman and i.r. spectroscopy of electrochemically obtained conducting and non-conducting poly(*N*-vinylcarbazole)

Mehmet Saçak*, Ural Akbulut†, Chunwei Cheng and David N. Batchelder
Department of Physics, University of Leeds, Leeds, LS2 9JT, UK
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The well resolved Raman spectra of electrochemically synthesized conducting and non-conducting poly(*N*-vinylcarbazole) were obtained. The Raman and i.r. spectra revealed that the conducting polymer had a 3,3′-dicarbazyl structure formed by dimerization at the 3,6 position and an appropriate mechanism was proposed. The conducting polymer was also obtained by electrolysis of the non-conducting polymer dissolved in dichloromethane. The conducting polymer obtained by this method was found to have a similar structure to that obtained by direct electrolysis of the monomer. The polymerization was monitored by the use of a specially designed cell, with *in situ* Raman spectra being taken from the electrode surface at different intervals. These spectra showed that there were no significant structural changes occurring in the conducting polymer during the polymerization process. In addition, the Raman image of the conducting polymer was taken by using the intense band which was located at $1600\,\mathrm{cm}^{-1}$.

(Keywords: poly(*N*-vinylcarbazole); electropolymerization; Raman spectroscopy)

INTRODUCTION

Owing to its interesting electrical and optoelectronic properties, the polymerization of *N*-vinylcarbazole (NVK) has been studied intensively. Free radical[1–3], cationic[4–6], Ziegler–Natta[7,8] and photochemical initiation[9,10] of NVK have all been reported. There are also a few reports on the electroinitiated polymerization of NVK, both by constant-current electrolysis[11–13] and by constant-potential electrolysis[14]. The latter polymerization technique has the advantage of induction by direct electron transfer from the monomer[14–18].

Electrolysis of NVK solutions usually coats the anode surface with a green conducting polymer, namely poly(NVK). The structure of this polymer coating has been studied by i.r. spectroscopy[19–21], cyclic voltammetry[20,22,23], u.v./vis. spectroscopy[24], and e.s.c.a.[21,25]. Thus far, there have been no reported Raman studies of the electroinitiated polymerization of NVK.

Raman spectra of polymer films prepared by electrolysis may be recorded without removing the film from the electrode; this is an advantage over many other analytical techniques. In addition, using a special cell, Raman spectra can be obtained *in situ* without disturbing the electrolysis process or damaging the polymer film. The use of Raman microprobe spectroscopy allows areas on the surface, as small as $1\,\mu\mathrm{m}^2$, to be studied[26]. The uniformity of the film can be observed directly by Raman spectroscopic imaging, a form of microscopy in which images of selected areas are recorded for light scattered in a selected Raman band[27]. Finally, the rate of polymerization can be followed by Raman studies of the solution[28].

In the present experiments, Raman spectra of poly(NVK) forming as green films on the electrode were obtained after electrolysis under various conditions. The Raman spectra of the non-conducting white poly(NVK) formed in solution are compared with those of the conducting green polymer film on the electrode. During electrolysis, an electrode initially coated with white poly(NVK) has been observed to convert to the green form. This process has been followed by *in situ* Raman spectroscopy, and Raman microscopy has been used to investigate the continuity of the films. In addition, Fourier transform infra-red (*FT*i.r.) spectra and electrical conductivities have been measured for the green poly(NVK) films that have been removed from the electrode.

EXPERIMENTAL

Materials

Acetonitrile (ACN) and dichloromethane (DCM) were purified using previously reported procedures[14]. *N*-vinylcarbazole (Aldrich) was crystallized twice from methanol, filtered and dried under vacuum. Tetrabutylammonium tetrafluoroborate (TBAFB) was used as received from Sigma.

Procedures

The H-type electrolysis cell has been described in detail previously[29]. The anode and cathode were Pt foils ($\mathrm{area}=1\,\mathrm{cm}^2$) and the reference electrode was a silver wire. A Princeton Applied Research (Model 362) scanning

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* Present address: Department of Chemistry, University of Ankara, 06100 Ankara, Turkey

† To whom correspondence should be addressed. Present address: Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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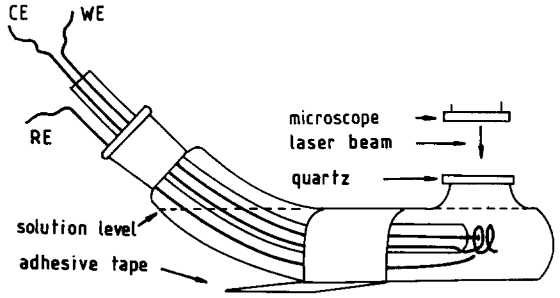

Figure 1 Schematic diagram of the electrolysis cell used for the *in situ* Raman measurements. The distance of the working electrode from the outer surface of the window is 8 mm; this permits use with a 20X ultra-long-working-distance Olympus microscope objective with a numerical aperture of 0.6: WE, working electrode; CE, counter electrode; RE, reference electrode

potentiostat was employed for the electrolyses. The white non-conducting poly(NVK) was obtained by the constant-potential electrolysis of an ACN solution containing 0.035 M NVK and 0.1 M TBAFB. The solution (50 ml) was purged with nitrogen for 15 min prior to electrolysis. The potential of the working electrode (anode) was adjusted to +2.0 V and the electrolysis was continued for 10 min. At the end of the electrolysis process, the precipitated polymer in the anolyte was washed with ACN and then dried under vacuum.

The conducting poly(NVK) formed as a green film on the surface of the Pt foil during electrolysis carried out under the same conditions as described above. This green film was also prepared from a DCM solution containing 0.035 M NVK and 0.1 M TBAFB with an electrolysis potential of +2.0 V.

The special electrolysis cell designed for *in situ* Raman microscopy studies and microprobe spectroscopy is shown in *Figure 1*. The maximum distance that the laser beam travelled through the solution to reach the polymer film on the anode was 8 mm. The working electrode was a 2 mm diameter Pt wire and the cathode was a 20 mm diameter coil of the same wire. A silver wire was used as a reference electrode. The cell was filled with a 5 ml solution of 0.035 M NVK and 0.1 M TBAFB in DCM to the level indicated in *Figure 1*. After the laser beam was focused on the surface of the working electrode with the aid of an optical microscope, the electrodes were connected to the potentiostat which had been adjusted to apply +2.0 V to the working electrode. Raman spectra of the green film forming on the Pt wire surface were obtained at various times during the electrolysis.

Raman spectra and images of poly(NVK) were recorded using a Renishaw Ramascope (Model 2000) with a 25 mW He–Ne laser. The spectral and spatial resolutions were 2 cm^{-1} and 1 μm, respectively. Spectra were recorded using laser power of ~0.5 mW at the specimen in order to avoid any degradation problems. Exposure times were typically 10 s for the spectra, and 30 s for the Raman images. Most of the spectra were recorded in air from films which had been removed from the electrolytic cell; some were recorded *in situ* using the cell shown in *Figure 1*. *FT*i.r. spectra were recorded of poly(NVK) dispersed in a KBr disc by using a Perkin–Elmer (Model 1710) spectrophotometer.

Conductivities of the green films of poly(NVK) which had been removed from the electrode were determined by using a four-probe measuring apparatus (with osmium tips). Current was passed through the two outer tips while the voltage drop was measured across the inner tips.

RESULTS AND DISCUSSION

When NVK is polymerized by free radical or cationic initiators, a non-conducting white polymer is obtained by the reaction path illustrated in *Figure 2*. During electroinitiated polymerization, white poly(NVK) is also obtained in solution (i.e. anolyte)[14,25]. The *FT*i.r. spectrum of the non-conducting white poly(NVK) obtained from the anolyte after electrolysis of a 0.035 M NVK solution in DCM solvent, which contained 0.1 M electrolyte (TBAFB), is shown in *Figure 3b*. During electrolysis the white poly(NVK) precipitated in the anode compartment while the anode surface simultaneously became coated with a green-black film. The polymerization of the NVK monomer to the white form of poly(NVK) proceeds via the vinyl groups. This structural change can be seen in the *FT*i.r. spectrum of

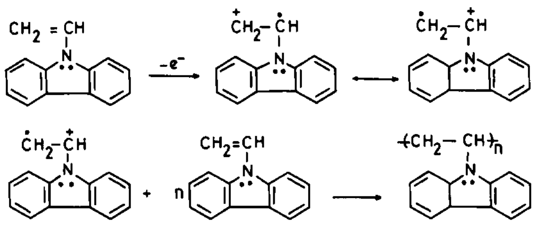

Figure 2 Suggested reaction path for the polymerization of NVK, by free radical or cationic initiators, to a non-conducting white polymer

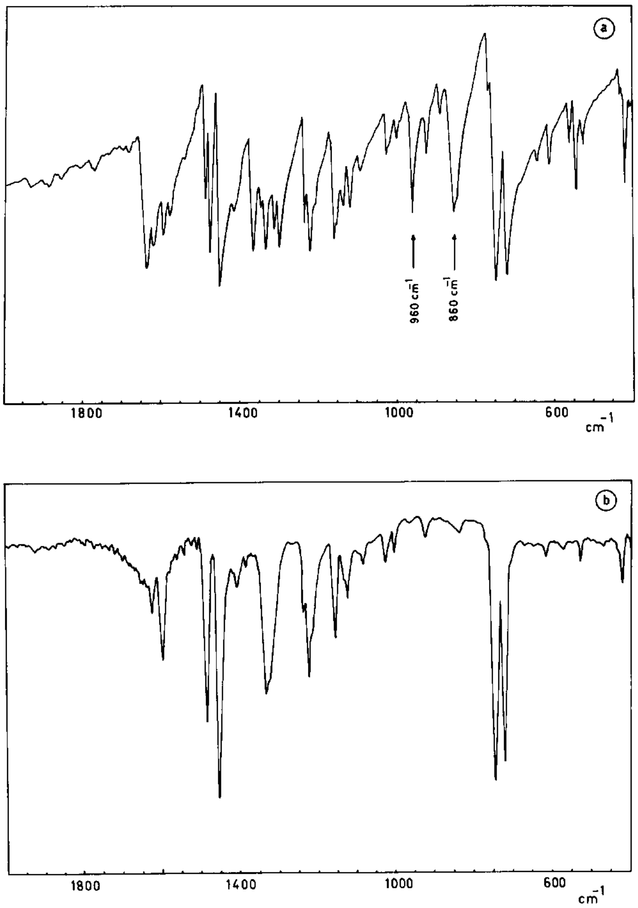

Figure 3 *FT*i.r. absorption spectra of (a) NVK monomer and (b) non-conducting white poly(NVK)

the polymer in *Figure 3b*; the vinyl bands of the monomer, at 860 and 960 cm^{-1}, are not present (see *Figure 3a*).

Figure 4 shows the Raman spectra of the monomer and the non-conducting white poly(NVK). The band at 1650 cm^{-1}, present in the Raman spectrum of the monomer, is attributed to the vinyl C=C stretching vibration. Absence of the 1650 cm^{-1} band in the polymer spectrum confirms that polymerization took place via the vinyl groups. Most of the other Raman bands of the monomer are also present in the Raman spectrum of the polymer, although there are differences in intensity and the Raman bands of the polymer are significantly broader.

Figure 5 shows the Raman spectrum of a conducting poly(NVK) specimen that was obtained as an anodic green film upon electrolysis of NVK in ACN. The film was washed in acetonitrile and dried while still on the Pt electrode, before the Raman spectrum was obtained. Essentially identical Raman spectra were obtained when DCM was used as the solvent; the use of this solvent has the advantage that the white polymer is soluble so that no precipitation was observed during electrolysis.

Conducting polymers can be doped by both chemical[30,31] and electrochemical[32,33] methods. Doping of poly(NVK) by $LiClO_4$[22] or tetra-n-butylammonium perchlorate[19,23] has been reported. Conducting polymers doped during electrolysis are partial cation radical salts where perchlorate or fluoroborate anions act as counter anions.

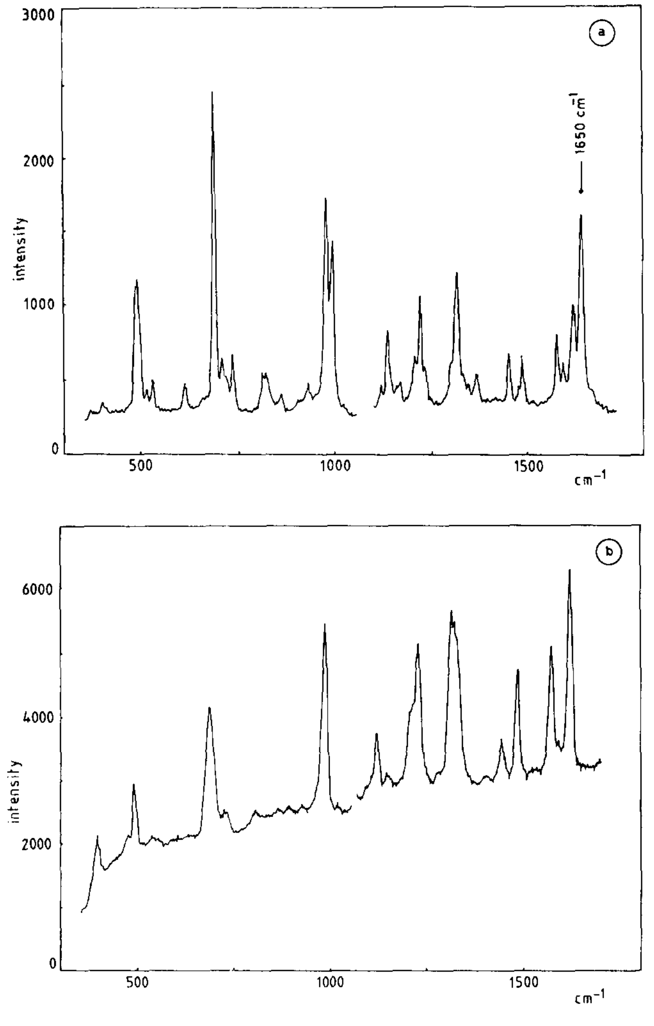

Figure 4 Raman spectra of (a) NVK monomer and (b) non-conducting white poly(NVK)

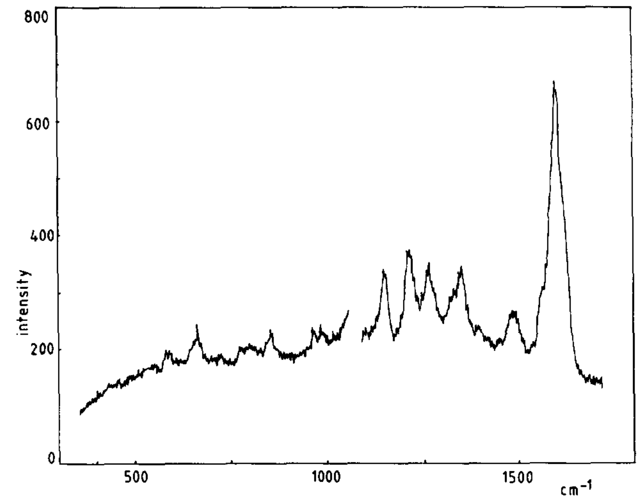

Figure 5 Raman spectrum of conducting green poly(NVK)

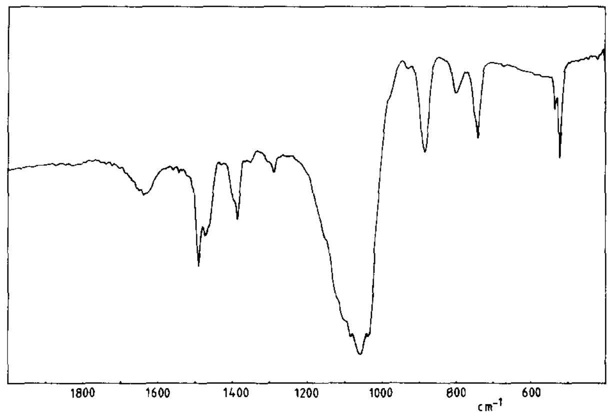

Figure 6 *FT*i.r. absorption spectrum of the TBAFB electrolyte

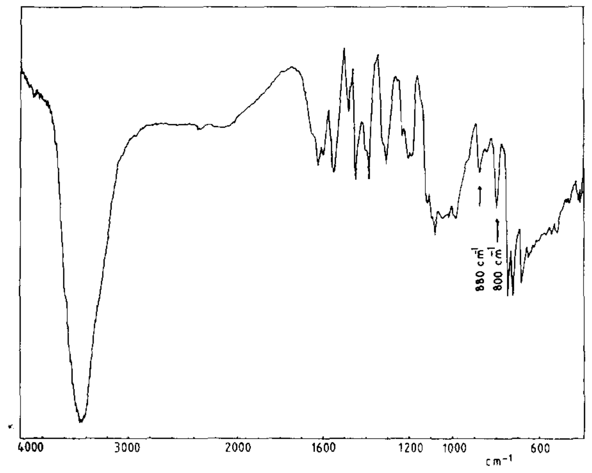

Figure 7 *FT*i.r. absorption spectrum of conducting green poly(NVK) dispersed in a KBr disc

For the conducting green polymers which we obtained on the anode, the BF_4^- anion should be the dopant. A band at 1100 cm^{-1} in the i.r. spectra of a green poly(NVK) film has been attributed to the presence of the ClO_4^- ion[20,22,25]. To date there has been no reported assignment of i.r. or Raman bands to the BF_4^- dopant in green poly(NVK).

We have measured the *FT*i.r. spectra of both TBAFB and green poly(NVK) dispersed in KBr discs; the results are shown in *Figures 6* and *7*, respectively. It can be clearly seen that a band at 1050 cm^{-1} appears in both spectra. This band does not exist in the *FT*i.r. spectra of NVK monomer or the white polymer (shown in *Figure 3*). Thus we tentatively identify the band at 1050 cm^{-1} with the presence of BF_4^- dopant in the green films.

The *FT*i.r. and Raman spectra of the green poly(NVK) film suggest the presence of 1,2,4-substituted benzene rings. Peaks at 800 and 880 cm^{-1} are present in the *FT*i.r. spectrum of the green polymer film (see *Figure 7*), but these are absent in the spectrum of the non-conducting white polymer (see *Figure 3b*). In the Raman spectrum of the green polymer film (*Figure 5*), bands attributed to 1,2,4-substituted benzene appear in the range 750–850 cm^{-1}.

These spectroscopic observations suggest that in the conducting green polymer, the vinyl group is not solely responsible for polymerization. The aromatic rings must also be involved in polymer propagation. The absence of spectral bands associated with 1,2,4-substituted benzene ring bands in the white polymers suggest that only the vinyl groups are involved in the polymerization. We therefore suggest that the reaction mechanism is as shown in *Figure 8*, the conversion of non-conducting poly(NVK) to the conducting form.

Various authors have suggested similar mechanisms where dimerization at the 3,6 position gives a 3,3′-dicarbazyl structure[12,21,22]. As seen in *Figure 8* the non-conducting white polymer which is produced from the monomer can then be oxidized to yield the conducting green polymer. In order to test the above mechanism we have designed some experiments to oxidize the white polymers electrochemically and then study their structures by *FT*i.r. and Raman spectroscopy. In one experiment, white poly(NVK) was dissolved in DCM containing only TBAFB (0.1 M) and electrolysis was carried out at +2.0 V. The anode surface was successfully coated with a green conducting polymer, although no monomer was present. As the electrolysis continued the growth of green polymer was monitored by Raman spectroscopy. In this experiment the dissolved (non-conducting) white polymer molecules must have been adsorbed on the surface of the anode and then oxidized. The polymer molecules are expected to travel towards the anode in the electrolysis solution.

In another experiment, the anode surface was coated with a film of white poly(NVK). The polymer was dissolved in DCM (2 wt%) and a few drops of the solution were placed on each side of the Pt foil anode, and the anode was then dried. The film-coated electrode was later immersed in ACN containing 0.1 M electrolyte, the white polymer being insoluble in the latter solvent. The film-coated electrode was used as the working electrode (anode) and electrolysis was carried out at +2.0 V. The white polymer film was gradually converted into a conducting green poly(NVK) film; the conversion was monitored by Raman spectroscopy. The Raman spectra of white, light green and dark green poly(NVK) films are given in *Figure 9*. The small band at 1600 cm^{-1} in the spectrum of the white polymer grows as the film is oxidized and becomes converted to the green form. The band at 1615 cm^{-1} is the major band in the spectrum of the white polymer; as the band at 1600 cm^{-1} becomes more intense, however, the band at 1615 cm^{-1} becomes hardly detectable.

In order to study the changes in the structure of poly(NVK) while the polymer was forming on the anode, the cell shown in *Figure 1* was used. It is known that the conductivity and structure of some conducting polymers change with time. Storing conditions, especially in air, can affect the structure of the conducting polymers. On the other hand, the structure of polymer on the surface and in the bulk may also be different. The conductivities are measured from the surface while the i.r. spectra are

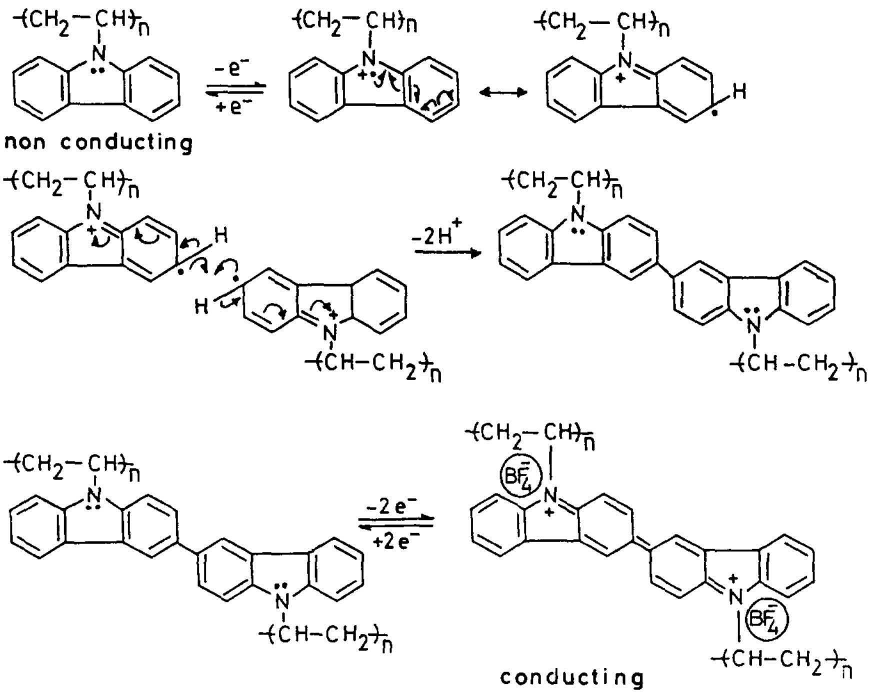

Figure 8 Suggested reaction mechanism for the conversion of non-conducting white poly(NVK) to the conducting green form

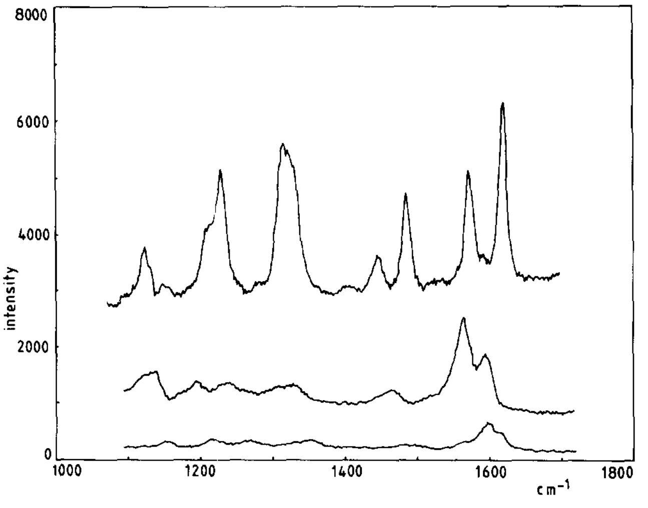

Figure 9 Raman spectra of poly(NVK) prepared initially as a white non-conducting film on the anode (top spectrum) and subsequently converted electrolytically, partially (middle spectrum) and, finally, completely, to the green conducting form (bottom spectrum)

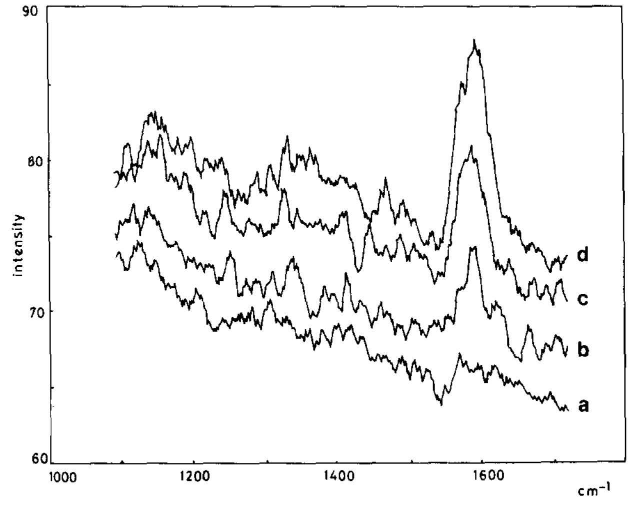

Figure 10 The *in situ* Raman spectra obtained during the formation of a conducting green film of poly(NVK) on the electrode shown for films obtained after various periods of electrolysis time: (b) 15 s; (c) 30 s; (d) 60 s. The spectrum of the bare Pt electrode (a) is shown as a reference: data have been subjected to an eleven-point smoothing function in order to show the band at 1600 cm^{-1} more clearly

usually obtained from bulk material in the form of a KBr disc. The powdered sample gives an average i.r. spectra of the surface and the bulk of polymer films. It is not easy to obtain *in situ* i.r. spectra from the surface of polymer films obtained by electrolysis, because of the small size of the electrodes and the opacity of the solution. In our case, our new system allowed us to obtain the Raman spectrum of conducting polymer films which were forming on very small diameter Pt wires, even at early stages of the reaction. Another advantage of our system was to be able to obtain the spectra of films at any point in the polymerization process as the reaction proceeded in the electrolysis solution.

Poly(NVK) films can be prepared either in ACN or DCM solution. We have preferred to use DCM for the simultaneous recording of *in situ* Raman spectra at the electrode since the white polymer forming in bulk is soluble in this solvent. When ACN is used as the solvent the precipitating white polymer causes scattering of the incident beam. The Raman spectra of bare Pt wire and the films coating the wire after 15, 30, and 60 s of electrolysis time are shown in *Figure 10*; in each case the exposure time was 10 s.

The film on the electrode had become so thick after 60 s of electrolysis that the focus was disturbed. The spectrum of the same area of film, obtained for 180 s of electrolysis time, after refocusing the microscope, is shown in *Figure 11*. Comparison of *Figures 5* and *11* shows that the spectrum of green poly(NVK) does not change significantly after 180 s of electrolysis. Another important observation was that the Raman spectra of the films obtained *in situ* are identical to those recorded from films that have been exposed to air for several hours (see *Figure 11*).

The four-probe conductivity of the green poly(NVK) film obtained after 10 min of electrolysis of 0.035 M NVK in DCM at +2.0 V was 1×10^{-4} S m^{-1}.

A Raman image of the film after 180 s of electrolysis time is shown in *Figure 12*. The image was recorded using light which had been scattered in the intense 1600 cm^{-1} Raman band of the green poly(NVK). Cracks, several micrometres across, can be seen in the otherwise uniform film. Clearly, great care needs to be taken in the

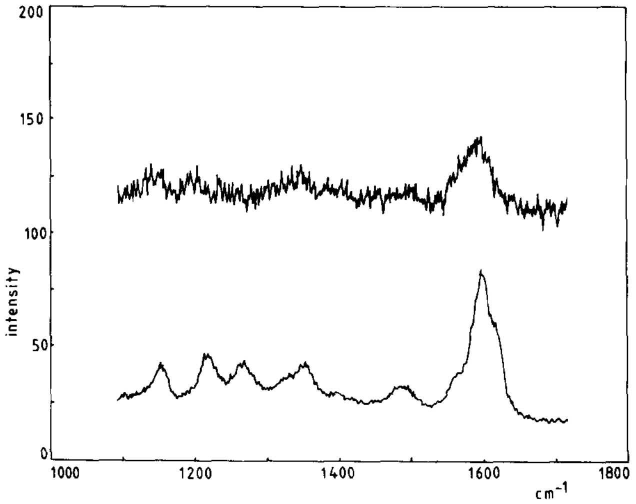

Figure 11 Raman spectrum of the same area of film as that used for *Figure 10*, recorded *in situ* after 180 s of electrolysis time (upper spectrum) compared to that recorded in air from a thick film which had been removed from the electrode (bottom spectrum, details from *Figure 5*)

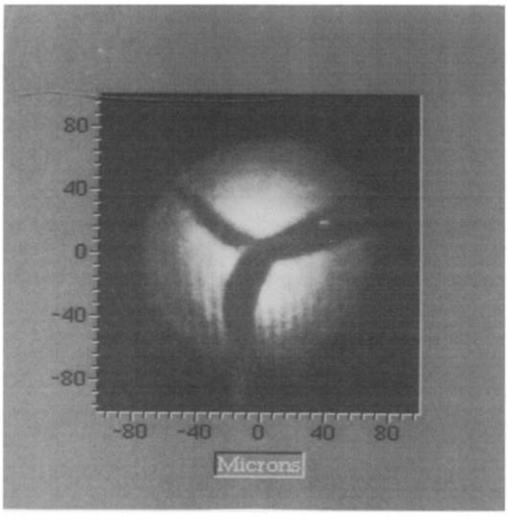

Figure 12 Raman image of green poly(NVK) after 180 s of electrolysis time, recorded *in situ*, using light in the 1600 cm^{-1} Raman band

interpretation of electrolysis data when using such polymer films as electrodes.

CONCLUSIONS

In conclusion, we have demonstrated that Raman microscopy and microprobe spectroscopy are useful tools for the study of the structures of conducting polymers forming on electrodes. Our system allowed us to study very thin films on small anodes which could not be removed from the electrode to be studied by other techniques. We have obtained evidence that the green conducting poly(NVK) may be formed by electrooxidation of white non-conducting poly(NVK). Well resolved Raman spectra of conducting poly(NVK) forming on the anode were obtained under various conditions.

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