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Characterization of electrochemically produced, two-component films of conducting polymers by Raman microscopy

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Platinum foil electrodes coated with a conducting polymer were used as working electrodes to deposit a second conducting polymer layer by electrolysis. Polyaniline/poly(*N*-vinylcarbazole), polypyrrole/poly(*N*-vinylcarbazole) and polypyrrole/polyaniline (or reverse order) films were synthesized on platinum foil electrodes by sequential electrolysis. These films were characterized by confocal Raman microprobe spectroscopy of both the solution and electrode sides of the films.

Depending upon conditions, either the second polymer was incorporated into the initially coated layer or a double-layer film was formed with a well-defined interface. Electrolysis of pyrrole and aniline monomer mixtures having molar ratios of pyrrole:aniline greater than 0.12 gave films rich in pyrrole. Polymerization of *N*-vinylcarbazole and pyrrole monomer mixtures, however, yielded only polypyrrole over a wide range of molar ratios. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: electropolymerization; conducting polymer films; Raman spectroscopy)

INTRODUCTION

Conducting polymers such as polypyrrole (PPy), polyaniline (PAn) and poly(*N*-vinylcarbazole) (PNvc) can readily be synthesized by electro-initiation and chemical initiators[1–6]. Recently the number of studies on the preparation and characterization of composites, copolymers and blends of conducting polymers has shown a significant increase. Chemical and electrochemical polymerization of two monomers whose individual homopolymers are conductive in origin may give a conducting product with different properties. It was reported that use of pyrrole as a comonomer during the polymerization of *N*-vinylcarbazole by $FeCl_3$ yielded a polymer which showed improved thermal stability and dielectric and conductivity characteristics compared to those of pure PNvc[7]. Electrochemical polymerization of pyrrole and thiophene was reported to yield a copolymer having electronic transport properties intermediate between those of the homopolymers[8]. The properties of copolymers, composites or blends of conducting polymers were found to depend on the proportion of monomers in the final product[8,9].

Conductive polymer composites, copolymers or blends may be obtained by electrolysing the solution of two monomers under suitable conditions or by first growing one conductive polymer on the surface of electrode as a film and later using that electrode for the polymerization of second monomer in a separate cell. In the latter method, the second monomer can penetrate into, and be electropolymerized within, the first layer. The extent of penetration may allow the second monomer to reach to electrode surface by diffusing through the first polymer layer. In this case it is difficult to characterize the interface between the two components of the polymer films[10].

It is possible to obtain a double-layer film having a well-defined interface by sequential electrochemical polymerization of monomers on metal electrodes under specific conditions. The polymer/polymer heterojunction may serve as a charge-trapping interface when the redox chemistry of the inner film occurs at a potential lower than that of the outer film[11–13]. Polymeric double layers can also be obtained by the selective electrolysis of an electrolytic solution containing monomers. Polymerization of pyrrole in the presence of thiophene has been carried out by adding pyrrole and lowering the voltage immediately after the electrochemical homopolymerization of thiophene had reached the desired extent[14]. It was pointed out that, at constant current, only pyrrole was electrochemically polymerized in the electrolytic solution containing pyrrole and thiophene as monomers[14]. In this technique, oxidation–reduction potentials of the monomers employed have to be relatively different.

Various techniques such as thermogravimetric analysis[7], infrared spectroscopy[8,9], scanning electron microscopy[9], u.v.–visible spectroscopy[8] and cyclic voltammetry[13] can be used in the characterization of two-component polymeric films. All these methods, however, reflect the bulk properties of the films. They do not give any information about the extent of interpenetration of the two layers.

Confocal Raman microprobe spectroscopy is a very useful technique for assessing the extent to which the second polymer diffuses into the first layer during the polymerization. Spectra can be recorded from scattering volumes of the order of 1 μm^3 without causing damage to the region concerned[15]. It is also possible to take *in situ* spectra during the polymerization without disturbing the progress of the polymerization by this method[16].

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In this study, Raman microprobe spectroscopy was used to characterize a series of two-component polymeric films. PPy/PAn, PPy/PNvc and PAn/PNvc (or reverse order) films were electrochemically obtained using sequential layering. Films were then peeled off, and the Raman spectra of both their solution and electrode sides were taken. Mixtures of aniline–pyrrole and non-conducting PNvc–pyrrole in various ratios were also electrolysed and characterized by Raman spectroscopy.

EXPERIMENTAL

Materials

All chemicals were supplied by the Aldrich Chemical Co. Aniline and pyrrole were distilled under reduced pressure immediately before use. Dichloromethane and tetrabutyl ammoniumtetrafluoroborate (TBAFB) were used as supplied. Non-conducting PNvc was synthesized by the electropolymerization of *N*-vinylcarbazole in acetonitrile at 1.5 V.

Procedures

Film production was carried out in an H-type electrolysis cell[17] at 1.0 V for 3–20 min. The working and counter electrodes were Pt foils of 1.0 cm^2 and 1.5 cm^2, respectively; the reference electrode was Ag/Ag$^+$. The double-component films were obtained as follows.

(a) *PAn/PPy and PPy/PAn films*: The electrode was first coated with PAn in a 50 ml aqueous solution of 1 M H_2SO_4 and 0.1 M aniline. The electrode was then transferred into a second cell containing 50 ml aqueous solution of 1 M H_2SO_4 and 0.1 M pyrrole, where it was coated with PPy. PPy/PAn films were prepared by reverse order of electrolysis.

(b) *PPy/PNvc and PNvc/PPy films*: The electrode was first coated with PPy in dichloromethane containing 0.1 M pyrrole and 0.1 M TBAFB. The electrode was then transferred into a second cell containing the dichloromethane solution of 0.1 M TBAFB and 2 g/100 ml non-conducting PNvc, where it was coated with PNvc. PNvc/PPy films were prepared by reverse order of electrolysis.

(c) *PNvc/PAn and PAn/PNvc films*: These films were prepared by two different methods. In the first method, the electrode was coated with PNvc as in (b) and then coated with PAn as in (a). In the second method, the electrode was first coated with PNvc as in (b) and then coated with PAn in an ethanol solution of 1 M H_2SO_4 and 0.1 M aniline. PAn/PNvc films were obtained by reverse order of electrolysis.

Some films were also obtained by the electrolysis of mixtures of aniline and pyrrole monomers in aqueous 1 M H_2SO_4 solution. Solutions of mixtures of non-conducting PNvc and pyrrole in dichloromethane and 1 M TBAFB were also electrolysed. Electrolysis was terminated when a visible colour change was observed (after 30–60 s) on the electrode surface. This resulted in non-peelable films less than 4 μm thick on the electrode surface. The Raman spectra of the films were taken directly from the electrode surface.

A Princeton Applied Research (PAR) Model 362 scanning potentiostat was used throughout the study.

Raman spectra were recorded using a Renishaw Raman microscope (Model 2000) with a 25 mW He–Ne laser and a 50 × objective. The spectral resolution was approximately 2 cm^{-1}. The confocal scattering volume was approximately a cylinder, 1 μm in diameter in the focal plane and 2 μm high[15].

RESULTS AND DISCUSSION

PAn/PPY and PPy/PAn films

PAn/PPy films were obtained by first coating PAn by the electrolysis in aqueous solution of 1 M H_2SO_4 and 0.1 M aniline, followed by coating with PPy in a different cell filled with an aqueous solution of 1 M H_2SO_4 and 0.1 M pyrrole. Freestanding films of approximately 12 μm thickness were peeled from the electrode. Raman spectra of the solution and electrode sides of PAn/PPy films are given in *Figure 1*. This figure also contains the Raman spectra of pure PAn and PPy synthesized under the same electrolysis conditions.

It can be seen in *Figure 1* that the spectrum of the solution side of PAn/PPy film (curve a) is similar to that of pure PPy (curve d). The spectrum of the electrode side (curve b), however, contains an additional Raman band at 1375 cm^{-1}, attributable to PPy, along with the main bands of PAn at

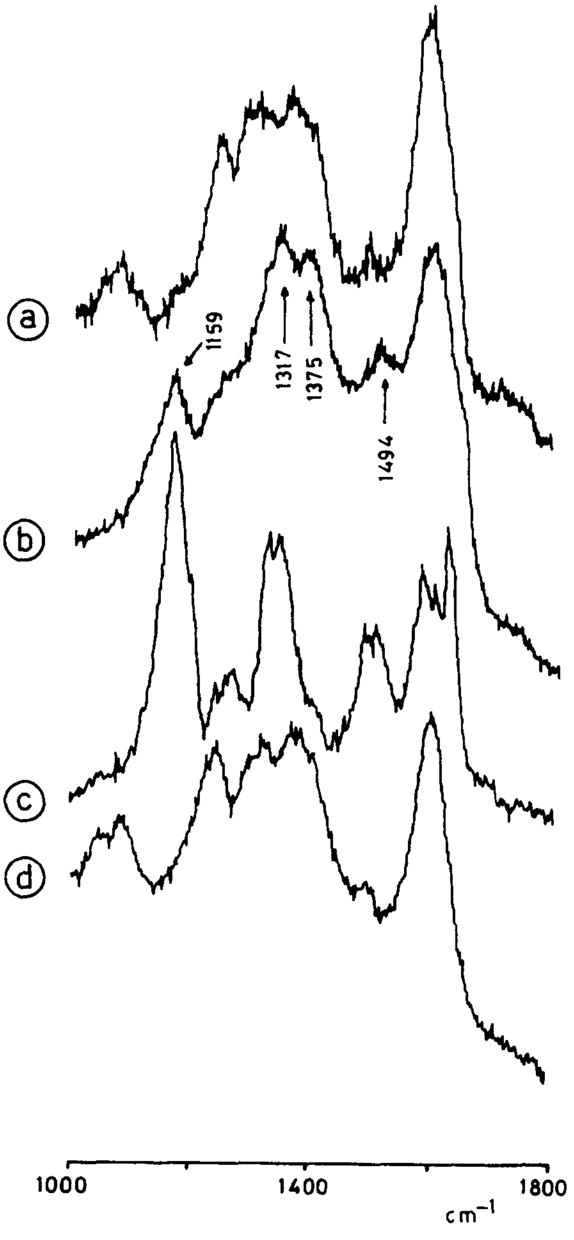

Figure 1 Raman spectra of the solution side (a) and electrode side (b) of a PAn/PPy film obtained by electrochemical coating of PAn followed by coating with PPy. For comparison, Raman spectra of films of pure PAn (c) and PPy (d) obtained by electro-initiated polymerization in water are also shown

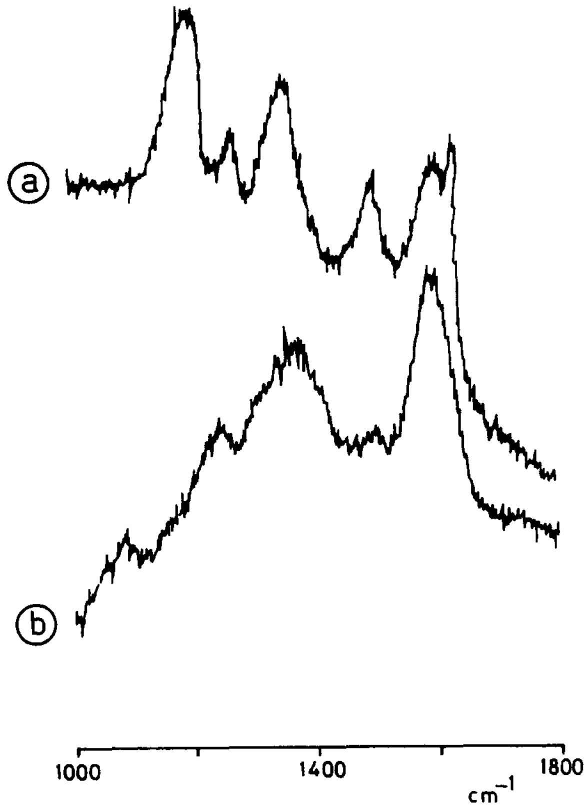

Figure 2 Raman spectra of the solution side (a) and electrode side (b) of a PPy/PAn film obtained by electrochemical coating of PPy followed by coating with PAn obtained by electro-initiated polymerization in water

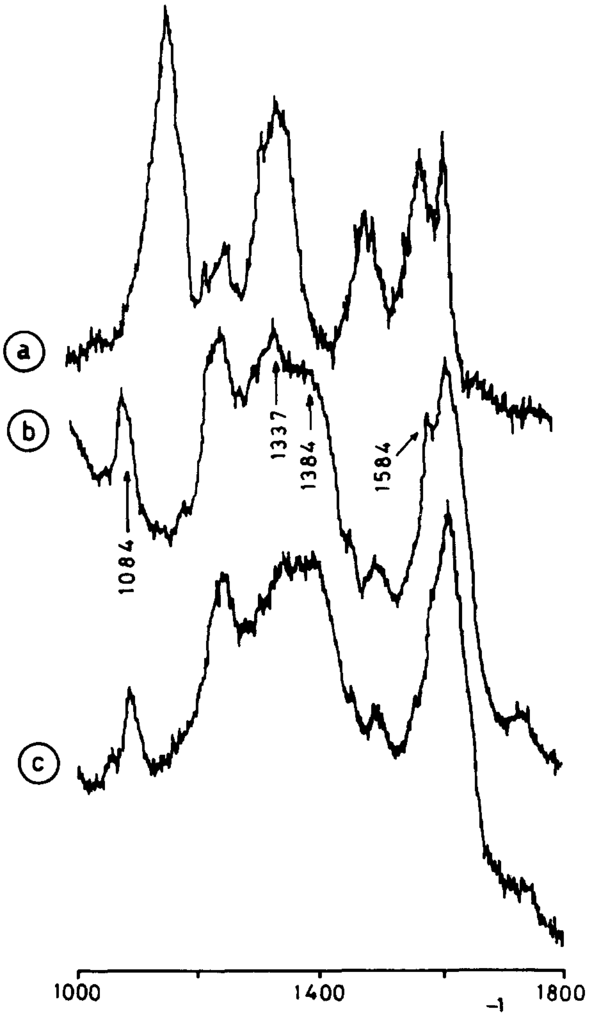

Figure 3 Raman spectra of PPy/PAn films obtained by the electrolysis of solutions having the following molar ratios of pyrrole:aniline: (a) 0.06, (b) 0.12, (c) 0.25

1159, 1317 and 1494 cm^{-1}. This shows that the PAn layer now contains a significant proportion of PPy. It is probable that pyrrole diffused through the PAn layer to the electrode surface where it was oxidized and polymerized, thus producing a polymer blend. It is also possible that pyrrole may have polymerized on the surface of the PAn layer and then grew into the PAn film, extending all the way to the electrode surface. In fact, the band at 1375 cm^{-1} was observed in the Raman spectrum of the electrode side of the film (curve b) within the first few seconds of the electrolysis of pyrrole; thus the second possibility is excluded and the experiment demonstrates that pyrrole can readily diffuse through a PAn film to reach the electrode surface.

Figure 2 shows the electrode and solution side spectra of a PPy/PAn film obtained under similar conditions to the PAn/PPy film, but in reverse order of electrolysis. The solution side (curve a) and electrode side (curve b) spectra are seen to be similar to those of pure PAn (curve c) and pure PPy (curve d), respectively, in *Figure 1*. This observation shows that aniline (or PAn) cannot diffuse into the initially coated PPy film to reach the electrode surface and, hence, that aniline oxidation takes place only on the PPy film.

Raman spectra of PPy/PAn films obtained by the electrolysis of solutions having different molar ratios of pyrrole and aniline are given in *Figure 3*. As seen from the figure, a spectrum (curve c) similar to that of pure pyrrole (curve c in *Figure 1*) was obtained when the pyrrole:aniline molar ratio exceeded 0.12. When this ratio was lower, the resulting spectrum (curve b) included the Raman bands at 1337 and 1584 cm^{-1} due to PAn plus those at 1084 and 1375 cm^{-1} due to PPy. The spectrum of a film produced with a 0.06 molar ratio of pyrrole:aniline (curve a) showed only the Raman bands of PAn. These observations suggest that both monomers can polymerize in the same media.

PNvc/PAn and PAn/PNvc films

Electrolysis of *N*-vinylcarbazole in solvents such as dichloromethane or acetonitrile results in the formation of green-coloured conducting PNvc and white-coloured non-conducting PNvc[18]. Non-conducting PNvc precipitates in acetonitrile while conducting PNvc coats the electrode surface. Electrolysis in dichloromethane also yields a green conducting PNvc film on the electrode surface, but the electrolysis solution remains homogeneous at the end of electrolysis since dichloromethane is a good solvent for non-conducting PNvc.

Conducting PNvc can be synthesized by electrolysis of a solution of dichloromethane containing dissolved non-conducting PNvc instead of monomer[16,19]. For these experiments, we produced conducting PNvc films on the electrode surface that were free of monomer contamination by the electrolysis of dichloromethane solution containing 0.2 g/100 ml non-conducting PNvc.

Green conducting PNvc films were formed on the electrode surface. Rapid vaporization of solvent occurred after the electrode was removed from the cell, leaving films that were brittle and disintegrated into small pieces. To prevent the films breaking up, the electrode was

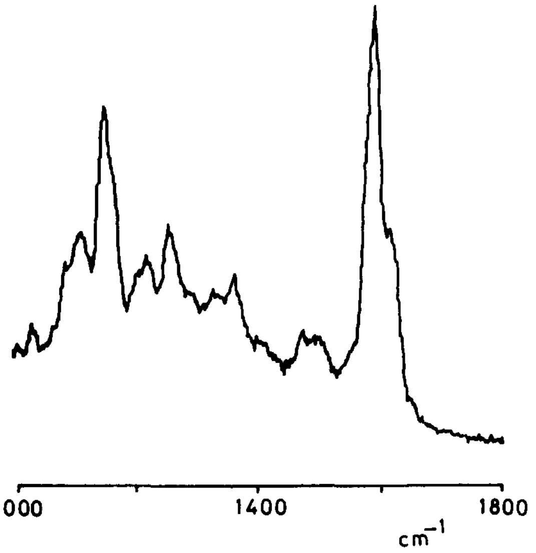

Figure 4 Raman spectrum of a PNvc film obtained by the electrolysis of a dichloromethane solution containing 0.2 g/100 ml non-conducting PNvc

immediately transferred to another cell containing a solution of 1 M H_2SO_4 and 0.1 M aniline. At the end of electrolysis, the films cracked into three or four large pieces, allowing us to take Raman spectra after the removal of the pieces from the electrode. The spectra of the solution and electrode sides of these parts were the same as those of pure PNvc shown in *Figure 4* and pure PAn shown in *Figure 1* (curve c), respectively. This indicates that aniline can polymerize on the PNvc layer surface before reaching the electrode surface.

PAn/PNvc films were obtained by reversing the order of electrochemical coating followed in the above procedure. The PAn-coated electrode was transferred into the cell where the PNvc coating was to be carried out while it was still wet. After the PAn/PNvc film was removed from the cell, it was observed that there was a dry PNvc layer on the solution side of the film due to rapid vaporization of dichloromethane and a wet PAn layer on the electrode side due to the aqueous medium. The spectra taken after the film was completely dried revealed that the spectrum of the electrode side of the film was similar to that of the pure PAn in *Figure 1* (curve c) whereas the spectrum of the solution side of the film was found to be similar to that of pure PNvc shown in *Figure 4*. It is thus possible to obtain films having well-defined interfaces by electrochemical coating carried out in two different media. The second coating was carried out in an organic medium; the first layer was prepared in an aqueous medium, thus preventing the polymer or monomer in the organic medium from diffusing into the wet film. The second monomer thus oxidized on the underlying polymer film, creating a double-layer film with a well-defined interface.

The experiment was repeated by transferring the PAn-coated electrode after complete removal of water from the film into the cell where PNvc coating was carried out. It was not possible, however, to peel the films obtained in this way off the electrode surface whereas the film easily peeled off in the former case. The spectrum of the electrode side thus could not be taken, but the Raman spectrum of the solution side was similar to that of pure PNvc (*Figure 4*).

We have also obtained films by successive electrolysis in two different organic media. First, a PAn layer was obtained by electrolysis in an ethanol solution of 1 M H_2SO_4 and 0.1 M aniline. A second layer of PNvc was then coated onto this film as described above. The preparation of PAn/PNvc films was carried out by reversing the order of electrolysis. In this way, easily peeled, robust and free-standing PNvc/PAn and PAn/PNvc films were obtained. The spectra of the solution sides of the PNvc/PAn films were observed to be the same as that of pure PAn obtained in ethanol (*Figure 5a*). The electrode side spectra (*Figure 5b*), however, contained Raman bands at 1326 and 1342 cm^{-1} due to PAn in addition to that at 1591 cm^{-1}, one of the main Raman bands of PNvc; this showed that the electrode side layer was not pure PNvc but a mixture of PNvc and PAn. As observed in the PPy/PAn films, the aniline may have diffused into the initial PNvc film to the surface of the electrode, oxidized there (or on the PNvc layer) and grown in PNvc to form a film of a polymer blend. By contrast, Raman spectra of electrode and solution sides of PAn/PNvc films obtained in ethanol/dichloromethane media were the same as those of the respective pure polymers (*Figures 4* and *5a*), indicating that a well-defined, double-layer film had formed.

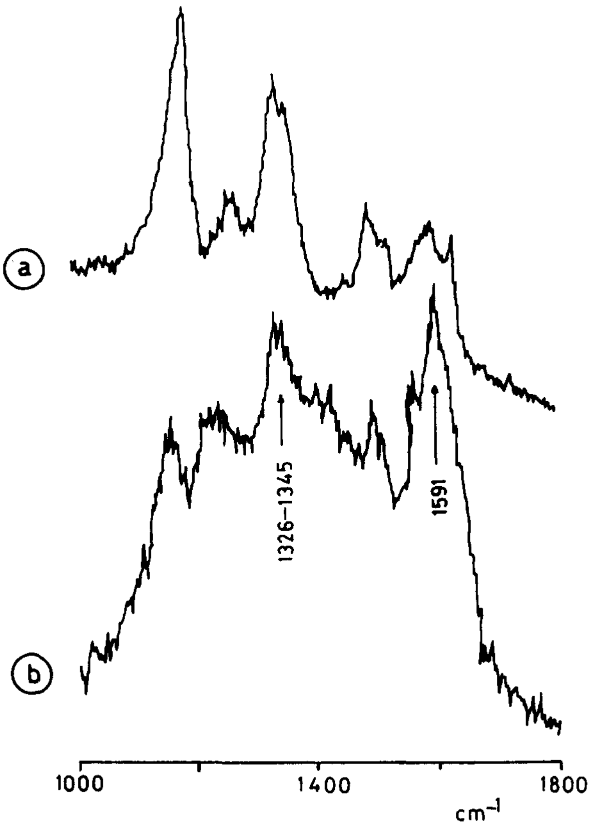

Figure 5 Raman spectra of (a) a pure PAn film obtained by the electrolysis of an ethanol solution of 1 M H_2SO_4 and 0.1 M aniline, and (b) the electrode side of a PNvc/PAn film obtained by first coating the electrode in a dichloromethane solution containing 0.2 g/100 ml non-conducting PNvc, followed by coating with PAn in a different cell filled with an ethanol solution of 1 M H_2SO_4 and 0.1 M aniline

PPy/PNvc and PNvc/PPy films

PPy/PNvc films were formed by first coating the electrode surface electrochemically with PPy in dichloromethane solution of 0.1 M pyrrole and 1 M TBAFB. The electrode was then transferred to a cell filed with a solution of 0.2 g non-conducting PNvc in 100 ml dichloromethane for the second electrolysis to deposit PNvc. The Raman spectra of the solution and electrode sides were the same, however, as that of the pure PPy spectrum given in *Figure 6*.

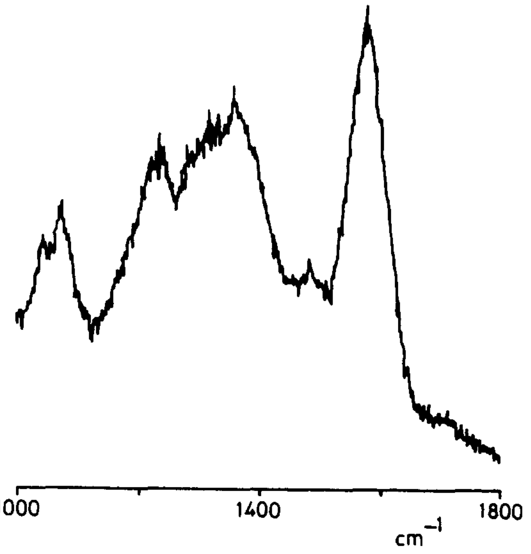

Figure 6 Raman spectrum of a PPy film obtained by the electrolysis of a dichloromethane solution of 0.1 M pyrrole and 0.1 M TBAFB

This result showed that under our experimental conditions it was not possible to coat PNvc onto the PPy film.

PNvc/PPy films were obtained by reversing the order of electrolysis. The resulting film was observed to be elastomeric, containing visible pores; it was not possible to peel the films from the electrode surface.

Films were also produced by the electrolysis of dichloromethane solutions containing pyrrole and non-conducting PNvc or pyrrole and *N*-vinylcarbazole mixtures having different molar ratios. The Raman spectra of the films obtained for all mixtures were the same as that of pure polypyrrole given in *Figure 6*. This result indicates that it is not possible to convert non-conducting PNvc to conducting PNvc (or *N*-vinylcarbazole to give PNvc) in the presence of pyrrole.

CONCLUSIONS

Confocal Raman microscopy is a useful technique for characterizing two-component polymeric films produced on the electrode surface by electropolymerization. This technique enables one to take the spectra of both sides of the films, with micron-scale spatial resolution, without causing any damage to the material.

Two types of film were observed when successive electrolysis in different solutions was carried out. In the case of PPy/PAn and PNvc/PAn films, with the first layer formed in an aqueous medium and the second by electrolysis in an organic medium, the second monomer polymerized onto the first polymer layer without reaching the electrode surface. Examination of the electrode sides of films such as PAn/PPy, however, showed the presence of Raman bands of both polymers; this indicated that there was substantial penetration of the second layer into the first.

The co-electrolysis of monomer mixtures also had two differing results. A mixture of pyrrole and *N*-vinylcarbazole proceeded as the homopolymerization of a single monomer since only the polymerization of pyrrole was observed. In contrast, mixtures of pyrrole and aniline produced films containing a blend of PPy and PAn.

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