In Situ IR Spectroscopic Study of Poly(*N*-vinylcarbazole) Film During Electrochemical Doping

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SYNOPSIS

In situ IR spectroscopic study was made on the electrochemical doping of poly(*N*-vinyl-carbazole) (PVK) by the subtractively normalized interfacial Fourier transform technique. The results show that the doping of ClO_4^- anion is limited by crosslinking of the polymer. The structure of doped PVK film depends on electrode potential and reaction time. Maximum doping of PVK may be achieved using a low oxidation potential for a proper reaction time. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The discovery of high electrical conductivity of polyacetylene upon doping[1] inspired vast scientific activity in the field of physics and chemistry of conducting polymers during the last decade.[2,3] Poly(*N*-vinylcarbazole) (PVK) can be doped both chemically and electrochemically, producing useful semiconductive material.[4,5] Although the conductivities of doped PVK are lower than that of others such as polypyrrole[6] or polythiophene,[7] it is an attractive material by virtue of its electrochromism and photoconductivity properties and applications for electrochromic displays,[8] polymer-modified electrodes,[9] lithium cells,[10] and electroreprography. Previous IR, ESCA, EPR,[11] UV-visible absorption,[12] and fluorescence emission[13] studies on PVK film deposited on a Pt surface showed that oxidized PVK contains C—C coupling at the carbon-3 position of the aromatic nucleus and carbazyl nuclei.[12]

However, *ex situ* measurement is not enough to study the structure change of the polymer during the electrochemical doping process. Due to advantages in obtaining information on the structure of species and radical ion intermediates at or near the electrode surface, *in situ* spectroelectrochemical measurement is a powerful method to determine the structural changes of a polymer during electro-

chemical redox processes. For instance, Sariciftci and Kuzmany[14] found clear evidence for two well-separated phase transitions of polyaniline (PANI) by *in situ* Fourier transform resonance Raman spectroscopy during electrochemical (ec) doping–undoping cycles.[15]

In this study, the *in situ* subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) measurement is used to characterize the doped PVK film and to study the film growth and structural change during the electrochemical doping process.

EXPERIMENTAL

PVK was used as received. Tetrabutylammonium perchlorate (TBAP) was vacuum dried at room temperature. Analytical grade dichloromethane was freshly distilled before used as solvent. The solution used for the preparation of doped PVK film contained $10^{-2}M$ PVK and $10^{-1}M$ TBAP used as the supporting electrolyte.

SNIFTIRS experiments were carried out with a Nicolet 730 FTIR apparatus. The working electrode was a platinum disk. A foil of platinized platinum was used as the counterelectrode and the reference electrode was a saturated calomel electrode (SCE). The infrared window used was a CaF_2 single crystal disk 2 mm thick. The incident light was at 60° to the surface of the IR window (Fig. 1). The potential of the working electrode was controlled by a model
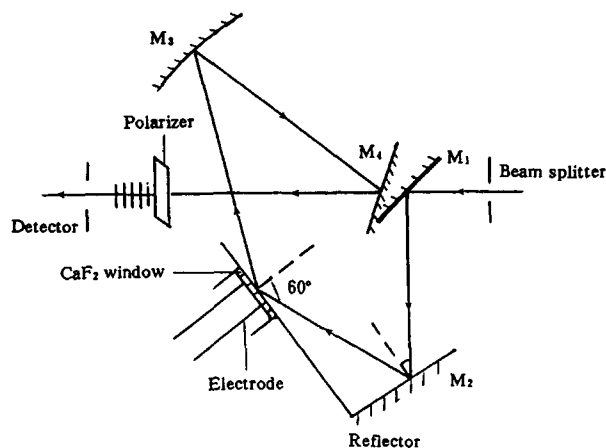
Figure 1 Beam geometry of SNIFTIRS measurement.

XHD-1 potentiostat. All spectra resulted from the accumulation of 400 interferometer scans at two different potentials and the treatment through $\Delta R/R = [R(E_2) - R(E_1)]/R(E_1)$, in which $R(E_1)$ and $R(E_2)$ represent single beam reflection spectroscopy at E_1 and E_2, respectively.

RESULTS AND DISCUSSION

Cyclic Voltammetric Behavior of PVK

The cyclic voltammograms of PVK oxidation leading to the formation of a doped polymer film at the Pt electrode surface are given in Figure 2. The oxidation of PVK starts at 1.1 V/SCE and, on the backsweep, gives rise to a reduction wave at 0.9 V. These waves can be ascribed to the formation and reduction of the carbazolylium cation radical. During the following cycles, the oxidation and reduction curves shift toward the less positive potentials; meanwhile, a reduction near 0 V becomes obvious and increases in intensity.

In Situ SNIFTIRS Study

Figure 3 shows the *in situ* spectra of doped PVK film. The reference potential E_1 was fixed at +0.26 V/SCE, which was the open-circuit potential of the system. The polarization potential E_2 was applied from −0.3 to +1.3 V/SCE. The spectra are significantly different in anodic and cathodic potential.

The spectral behavior observed for anodic potentials characteristic of the doping form of PVK film corresponding to the charge-transfer complex between the carbazolylium cation radical and the anion. The bands at 1610, 1570, and 1491 cm⁻¹ can be

ascribed to the C=C stretch of the carbazyl ring corresponding to carbazolylium cation radicals, and the bands observed at 1398 and 1310 cm⁻¹ are assigned to the C—N vibration of the doped PVK film. These bands are associated with the bands at 1134 and 1064 cm⁻¹ related to the incorporation of ClO_4^- counterions. An increase of the absorption intensities with increasing anodic potential ($E_2 \leq +1.2$ V/SCE) is observed for all bands, and there are significant shifts around 1570, 1310 cm⁻¹ to higher frequencies, indicating a change in the carbazyl ring structure. Negative bands at 3052, 2964, and 2896 cm⁻¹ ascribed to the C—H stretching vibrations of the carbazyl ring and chain, in which the C—H vibrational absorption of the cation from the supporting electrolyte is combined, are from the loss of groups at the more positive potential. It is worth noting that, as the polarization potential was modulated to $\geq +1.3$ V, all band intensities began to decrease, which indicates a net loss of the electroactive substances containing carbazolylium cation radicals. This can be interpreted from the gradual crosslinking of polymer with the loss of protons, accompanied by the release of ClO_4^- anions. The protons could be reduced into H atoms and this reduction generated a small current near 0 V in the cyclic voltammogram (see Fig. 2). The results of Figure 3(a) show that the 1.2 V oxidized form of PVK has the maximum doping level. In addition, the background absorption increases with increasing doping degree, which probably originates from changes of the electronic structure. According to the structural model proposed by Sariciftci et al.,[16] a counterion complexation between the alkyl side chain and the conducting PVK backbone lead to the charge local-

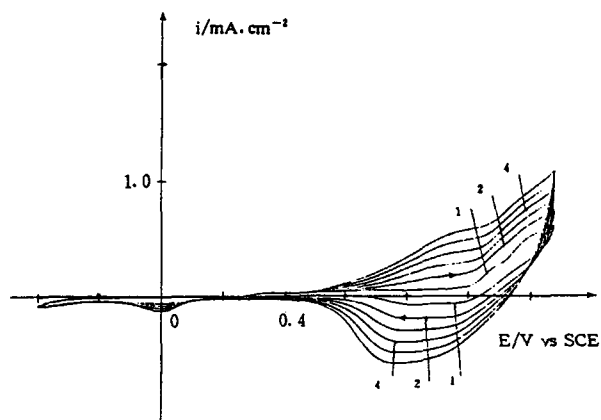**Figure 2** Cyclic voltammogram of PVK oxidation at a Pt electrode in PVK (0.01M) + TBAP (0.1M) dichloromethane solution at a sweep rate of 10 mV s⁻¹.
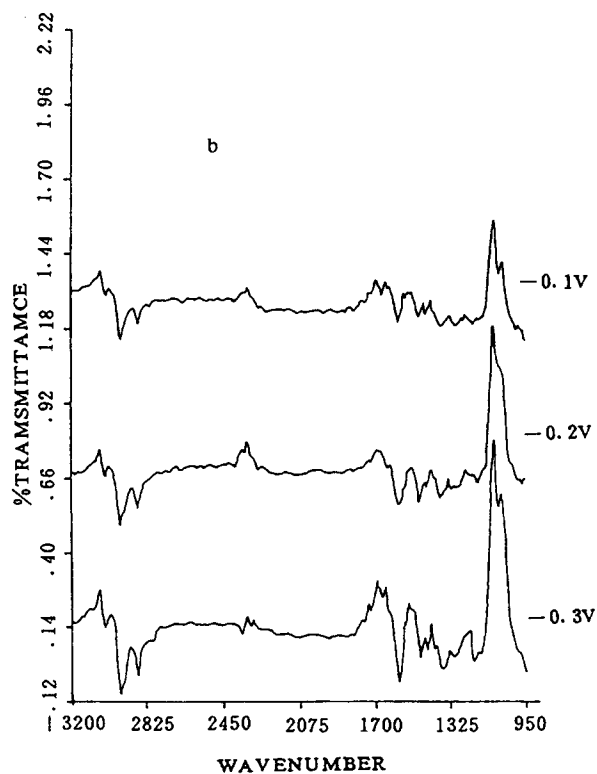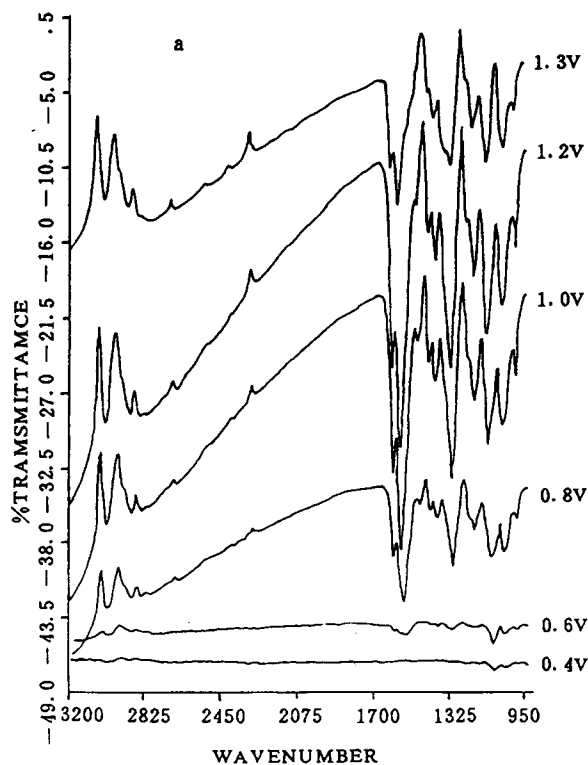
ization, and thereby the higher IR-activated vibration (IRAV) frequencies.

On the contrary, the spectral behavior observed for cathodic potential is characteristic of the undoping form of PVK film. The bands related to the incorporation of ClO_4^- disappear; whereas the negative bands at 1108 and 1068 cm^{-1} due to the release of ClO_4^- from the polymer matrix are observed with the enhancement of increasing cathodic potential. The bands at 3030, 2960, and 2872 cm^{-1} are mainly characteristic of the vibration of the carbazyl ring and chain in the neutral state. The $C=C$ bands at 1590, 1482, and 1442 cm^{-1} and the $C-N$ bands at 1368 and 1302 cm^{-1} are quite different from those of the doping state. The large changes in the $C=C$ and $C-N$ vibrational frequencies denote a carbazyl ring structural transition. That is to say, the imposition of a cathodic potential resulted in undoping of the doped PVK film.

Figure 4 represents the *in situ* spectra of the system Pt electrode in CH_2Cl_2 + PVK $(0.01M)$ + TBAP $(0.1M)$. It shows the adsorption layer at the electrode surface. The reference potential E_1 was fixed at +0.21 V/SCE, which was the open-circuit potential of the system. The polarization potential
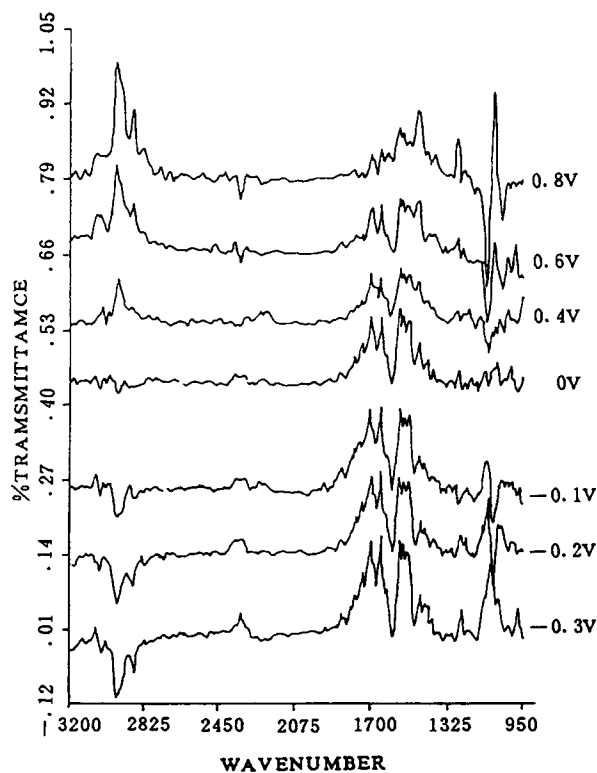

Figure 3 *In situ* spectra of doped PVK prepared at a constant potential of 1.3 V/SCE for 10 min. Medium: CH_2Cl_2 + TBAP $(0.1M)$. Reference potential: E_1 = +0.26 V/SCE. (a) $E_2 > 0$ V and (b) $E_2 < 0$ V.

Figure 4 *In situ* spectra for the system CH_2Cl_2 + PVK $(0.01M)$ + TBAP $(0.1M)$ at various potentials. Reference potential: E_1 = +0.21 V/SCE.
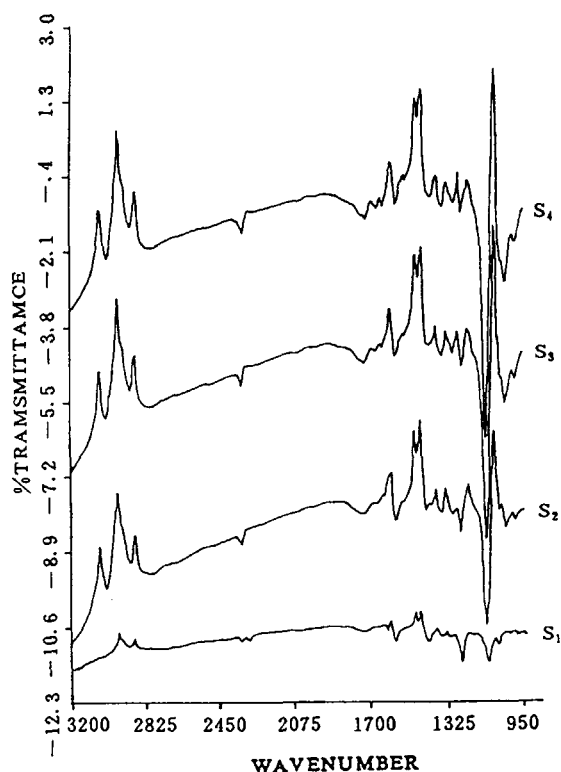
Figure 5 *In situ* spectra during electrochemical doping of PVK at a constant potential of 1.3 V/SCE; each spectrum was recorded after 5 min. Medium: the system following Figure 4.

E_2 was modulated from the spectra; three main regions of spectra around 3000, 1500, and 1100 cm^{-1} are clearly observable. The C — H stretching vibration around 3000 cm^{-1} comes from PVK and electrolyte cations, and the loss of these species increases with increasing positive potential. With respect to the C = C vibration of the adsorbed PVK prepolymer, the 1590-cm^{-1} band disappeared at 0.8 V; the 1478 cm^{-1} band changed from positive to negative at 0.6 V and its loss of absorption intensity was increased continuously. The ClO_4^- vibration absorption around 1100 cm^{-1} was also found with the phase change during modulating potential. Under the cathodic potential, the negative band at 1104 cm^{-1} indicates a reduction in adsorption of ClO_4^- anion; when the potential was modulated toward positive, the positive band at 1121 cm^{-1} with a enhancement of absorption intensity indicates an increase of ClO_4^- anion adsorption.

Figure 5 shows the *in situ* spectra of the electrochemical doping of PVK at a constant potential of 1.3 V/SCE. It is observed that the adsorption of ClO_4^- continued to increase as does the loss of absorption intensity around 1478 cm^{-1}. The 1570-cm^{-1}

band assigned to the C = C stretching vibration of the carbazyl ring in the doping state is visible. It is necessary to state that to obtain the largest reflection energy of IR irradiation the working electrode was pressed to the window, so there were few reactants at the electrode surface and the doping reaction was very slow. As shown in the figure, the spectral peaks of doped polymer occurred slowly.

Further experiments were performed to overcome the above problems. The solution on the electrode surface was renewed after the spectra were recorded every 5 min (Fig. 6). In this case, the band intensities of doped polymer increased rapidly, especially for the 1570-cm^{-1} band and the 1310-cm^{-1} band, and the resulting spectra were in good agreement with that in Figure 3(a). It could be observed that the v_3 vibration of ClO_4^- around 1100 cm^{-1} split off one low-frequency band while shifting to higher frequencies with the progress of the oxidation process, which may be due to the interaction between PVK and ClO_4^-. Furthermore, an analogous phenomenon with Figure 3(a) is observed: the band intensities reached the maximum after a period of time and began to decrease. This predicts that the crosslinking of polymer exceeded the production of carba-
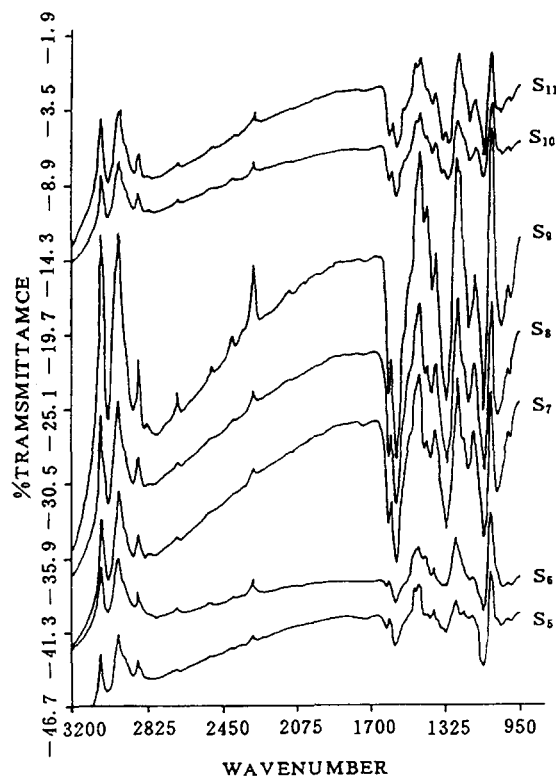

Figure 6 Continuation of Figure 5, the solution of the electrode surface was renewed after the spectra were recorded once every 5 min.

zolylium cation radicals. Due to the crosslinking of polymer, the electrochemical doping of PVK has a doping threshold under a low oxidation potential and a proper reaction time. At this moment, the doped PVK possesses the maximum concentration of carbazolylium cation radicals and thereby the maximum doping level. Increasing anodic potential or prolonging reaction time would increase the crosslinking degree of the polymer, and then reduce the concentration of carbazolylium cation radicals and the doping degree of ClO_4^-.

CONCLUSION

An *in situ* IR spectroscopy measurement provided the initial results of the electrochemical doping process of PVK. It was found that the structure of the doped PVK film depends on the electrode potential and reaction time. Due to the crosslinking of the polymer, the electrochemical doping of PVK has a threshold at which the doped PVK possesses the maximum doping level.

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