

# Electrochemical Synthesis of Poly(*N*-vinyl carbazole) Doped with HSO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> Anions

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**ABSTRACT:** In this study, the conducting forms of poly(*N*-vinyl carbazole) (PNVC) doped with HSO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> anions were synthesized electrochemically in dioxane and ethanol. It was observed that the acid concentration was an important factor in the synthesis of the conducting PNVC in dioxane–H<sub>2</sub>SO<sub>4</sub> media. No conducting PNVC film was formed on the electrode surface in the electrolyses carried out with acid concentrations below 2.0 M H<sub>2</sub>SO<sub>4</sub> in dioxane. However, a conducting PNVC film was obtained at lower acid concentrations (i.e., 0.5 M H<sub>2</sub>SO<sub>4</sub>) when the solvent was switched from dioxane to ethanol. The use of HCl and acetic acid at different concentrations in ethanol or dioxane media failed to yield conducting PNVC. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1792–1796, 1999

**Key words:** conducting polymers; poly(*N*-vinyl carbazole); doping; Raman spectroscopy

## INTRODUCTION

Although the conductivity of poly(*N*-vinyl carbazole) (PNVC), about 10<sup>-6</sup> S/cm,<sup>1,2</sup> is lower by several orders of magnitude than that of polypyrrole,<sup>3,4</sup> polythiophene,<sup>5</sup> or polyaniline<sup>6,7</sup> (which are each on the order of 1–10<sup>2</sup> S/cm), some of its properties, including electrochromism, photoconductivity, and thermal stability,<sup>8,9</sup> make it attractive in many respects. The polymerization of *N*-vinyl carbazole (NVC) can be carried out using free-radical initiators<sup>10,11</sup> and cationic initiators.<sup>12,13</sup> Attempts to polymerize NVC by anionic initiators have not been successful.<sup>14</sup> PNVC can also be synthesized by electro-initiated polymerization under constant current or potential.<sup>15,16</sup> Electropolymerization enables deposition of a conducting form of PNVC as a film onto the working electrode surface.<sup>17–20</sup>

The electrochemical synthesis of PNVC in acid medium has been reported by Cattarin et al.,<sup>18</sup>

who stated that the dopant anion of the conducting PNVC obtained in aqueous HClO<sub>4</sub> was ClO<sub>4</sub><sup>-</sup>. The type of dopant anion effects certain properties of the conducting polymers, including electrical conductivity, thermal and storage ability, morphology, and polymerization rate.<sup>21–24</sup> Therefore, investigation of the effect of various dopants on the polymerization and properties of conducting polymers is quite important from a scientific standpoint.

This study concerns electrochemical synthesis of the conducting PNVC doped with HSO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> and its characterization by Raman microscope spectroscopy. The literature includes various reports on the characterization of PNVC by IR spectroscopy,<sup>15,25</sup> cyclic voltametry,<sup>17,18,26</sup> ultraviolet-visible (UV-vis) spectroscopy,<sup>8</sup> and electron spectroscopy for chemical analysis (ESCA).<sup>27</sup> However, the use of Raman spectroscopy has been limited. Some results of electro-initiated polymerization of NVC monitored by Raman spectroscopy have been reported in recent studies.<sup>20</sup> Raman spectra of polymer films can be recorded without removing the film from the electrode surface, a

great advantage over other analytical techniques. The use of Raman microprobe spectroscopy allows the study of surface areas as small as  $1 \mu\text{m}^2$ .<sup>28</sup>

## EXPERIMENTAL

### Materials

*N*-vinyl carbazole (NVC; Aldrich, Steinheim, Germany) was crystallized from methanol, filtered, and dried under vacuum. Other chemicals such as ethanol, dichloromethane, dioxane (Aldrich, Steinheim, Germany), and tetrabutylammonium tetrafluoroborate (TBAFB; Sigma, St. Louis, USA) were used without further purification.

### Procedures

The H-type electrolysis cell has been described in detail in earlier work.<sup>29</sup> The anode and cathode were Pt foils, and the reference electrode was  $\text{Ag}^0/\text{Ag}^+$ , in the form of an isolated Luggin capillary. The electrolyses were carried using an EG&G Princeton Applied Research (PAR) Model 362 scanning potentiostat.

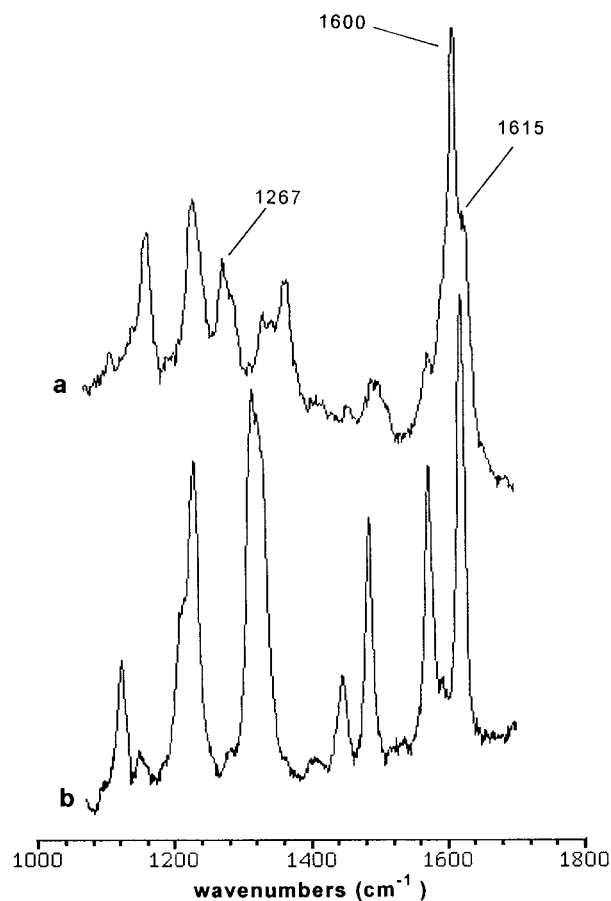
The white-colored nonconducting PNVC was obtained by the constant-potential electrolysis of an 50 mL of acetonitrile solution containing 0.01 M NVC and 0.1 M TBAFB. The solution was purged with nitrogen for 15 min prior to electrolysis. The potential of the working electrode was adjusted to +1.8 V, and electrolysis was continued for 10 min. At the end of electrolysis, the precipitated polymer in the anolyte was filtered off, washed with acetonitrile, and dried under vacuum.

Raman spectra were recorded using a Renishaw model 2000 Raman microscope with a 25-mW He-Ne laser and 50X objective. The spectral resolution was approximately  $2 \text{ cm}^{-1}$ . The confocal scattering volume was approximately a cylinder,  $1 \mu\text{m}$  in diameter in the focal plane and  $2 \mu\text{m}$  in height.<sup>30</sup>

Conductivities of the films were determined using a four-probe measuring apparatus with osmium tips. The current was passed through the outer tips, and the voltage drop was measured across the inner tips. The samples collected after a certain number of electrolyses were pelleted under a pressure of 10 MPa.

## RESULTS AND DISCUSSION

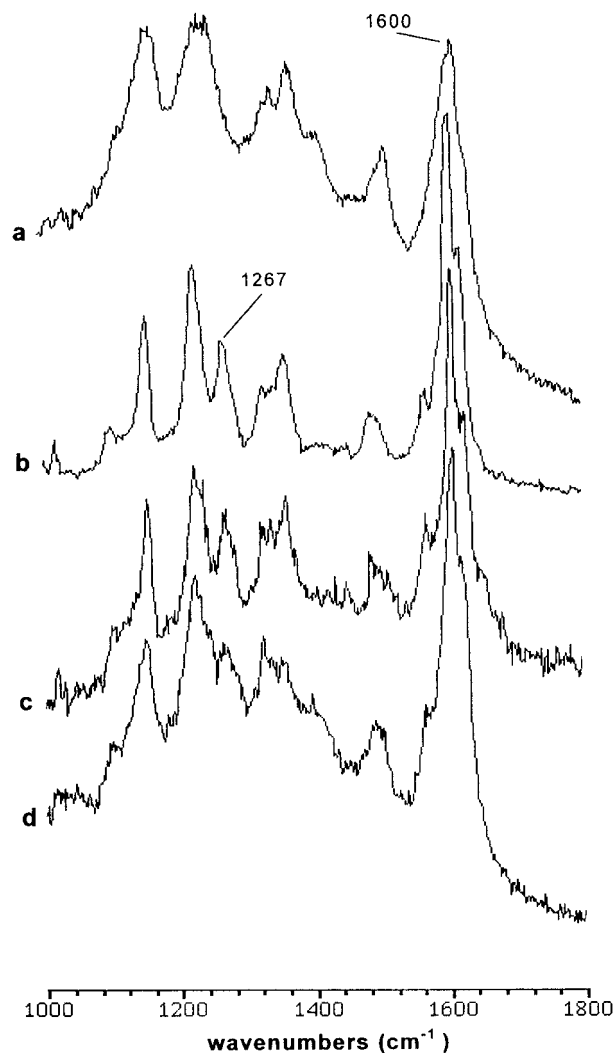
Electrolysis of NVC in organic solvents such as dichloromethane and acetonitrile results in the



**Figure 1.** Raman spectra of (a) conducting PNVC obtained electrochemically in dichloromethane containing 0.01 M NVC and 0.1 M TBAFB and (b) nonconducting PNVC.

formation of white-colored nonconducting PNVC and green-colored conducting PNVC.<sup>21,28</sup> The nonconducting PNVC precipitates in electrolyte solution; the conducting PNVC covers the electrode surface as a green-colored film. Electrolysis in dichloromethane yields a green-colored conducting PNVC film on the electrode surface, and the electrolyte solution contains dissolved nonconducting PNVC, because dichloromethane is a good solvent for the nonconducting PNVC.

Figure 1a shows the Raman spectrum of green-colored conducting PNVC formed on the electrode surface as a result of the electrolysis of 0.01 M NVC in dichloromethane containing 0.1 M TBAFB. This spectrum was discussed in an earlier study, where it was investigated in detail by comparing it to the spectrum of nonconducting PNVC<sup>20</sup> [see Fig. 1(b)]. It is known that the peak observed at  $1615 \text{ cm}^{-1}$  is the major band in the Raman spectrum of nonconducting PNVC. This



**Figure 2.** Raman spectra of conducting PNVC obtained electrochemically in (a) dioxane containing 0.01 M NVC and 2.0 M  $\text{H}_2\text{SO}_4$ , (b) ethanol containing 0.01 M NVC and 1.0 M  $\text{H}_2\text{SO}_4$ , (c) ethanol containing 0.01 M NVC and 1.0 M  $\text{HNO}_3$ , and (d) pure  $\text{H}_2\text{SO}_4$  containing 0.01 M NVC.

peak becomes barely detectable, and the peak at  $1600\text{ cm}^{-1}$  becomes more intense in the Raman spectrum of the conducting form<sup>20</sup> [see Fig. 1(a)].

Dioxane was chosen as a solvent for the polymerization of NVC in  $\text{H}_2\text{SO}_4$  media, because it is a good solvent for both the NVC and the nonconducting PNVC. The polymerization of NVC in the dioxane- $\text{H}_2\text{SO}_4$  media yields nonconducting PNVC dissolved in the bulk of the solution and conducting PNVC film deposited on the electrode surface.

Figure 2(a) illustrates the Raman spectrum of the film formed on the electrode surface after electrolysis of 0.01M NVC in dioxane containing 2.0 M

$\text{H}_2\text{SO}_4$  at a potential of 1.0 V. The peak observed at  $1267\text{ cm}^{-1}$  in the spectrum of PNVC obtained in dichloromethane-TBAFB media [see Fig. 1(a)] disappeared in the dioxane- $\text{H}_2\text{SO}_4$  media [see Fig. 2(a)]. Other characteristic peaks are similar.

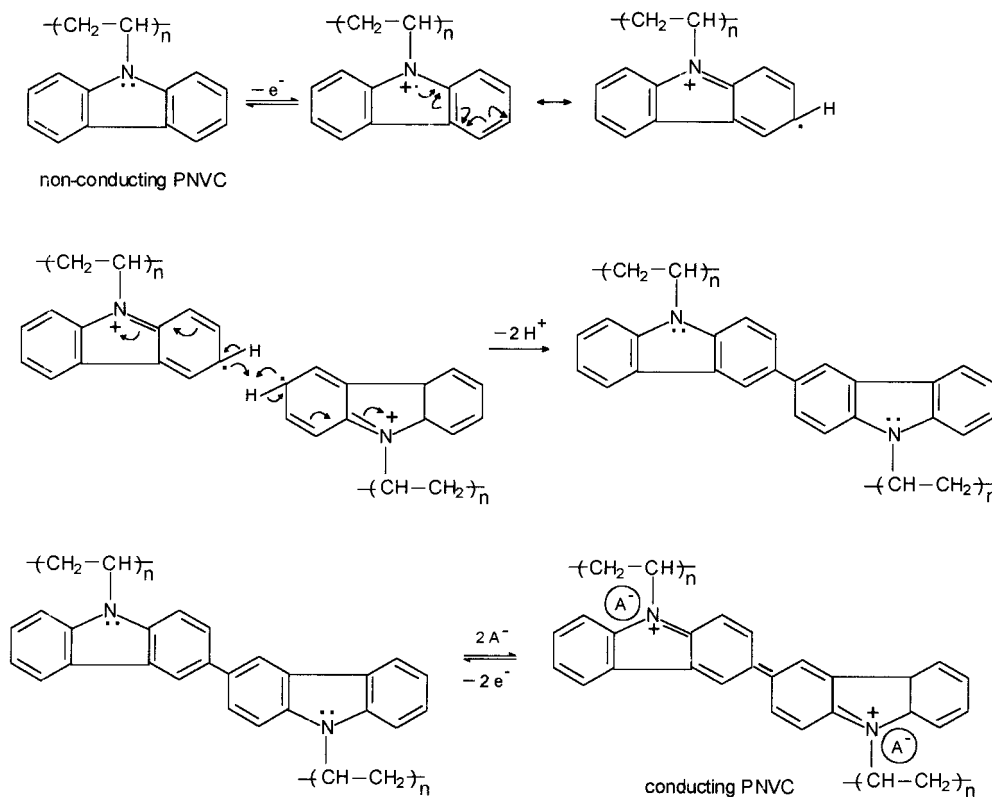
The experimental results show that acid concentration is an important factor in the synthesis of the conducting PNVC in dioxane- $\text{H}_2\text{SO}_4$  media. No conducting PNVC was formed on the electrode surface in electrolyses done with acid concentrations below 2.0 M  $\text{H}_2\text{SO}_4$ . However, conducting PNVC was formed at lower acid concentrations when the solvent was switched from dioxane to ethanol. The fact that polymerization occurs at a lower acid concentration in ethanol than in dioxane may be attributed to the greater dissociation of acid in ethanol.

The polymerization of NVC in ethanol- $\text{H}_2\text{SO}_4$  media showed a similar behavior as that done in acetonitrile, forming a conducting PNVC on the electrode surface while the nonconducting white-colored PNVC precipitated out. Raman spectra of nonconducting PNVC obtained in dioxane- $\text{H}_2\text{SO}_4$  and ethanol- $\text{H}_2\text{SO}_4$  media were found to contain the basic peaks of PNVC obtained in dichloromethane-TBAFB [see Fig. 1(b)].

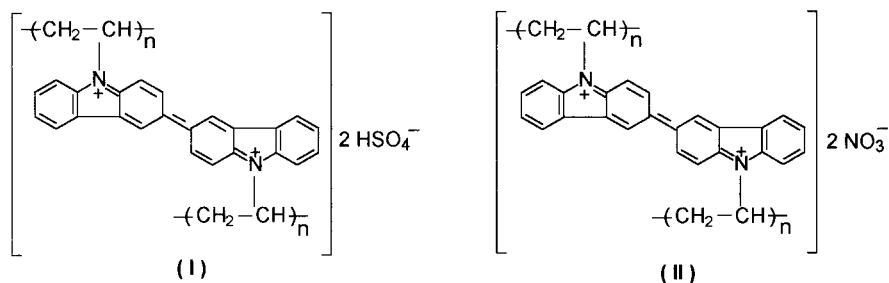
The Raman spectrum of conducting PNVC obtained by the polymerization of 0.01 M NVC in ethanol-1.0 M  $\text{H}_2\text{SO}_4$  media at 1.0 V is given in Figure 2(b). Although the dopant anions are different, the Raman spectra obtained in ethanol- $\text{H}_2\text{SO}_4$  and dichloromethane-TBAFB media are similar [see Figs. 1(a) and 2(b)]. It is also possible to obtain conducting PNVC in ethanol-0.5 M  $\text{H}_2\text{SO}_4$  media at 1.0 V.

In another experiment, electrolysis was done in ethanol by changing the acid, using 1.0 M  $\text{HNO}_3$  instead of 1.0 M  $\text{H}_2\text{SO}_4$ . The Raman spectrum of the PNVC obtained in ethanol- $\text{HNO}_3$  media is shown in Figure 2(c). This spectrum contains the basic peaks of PNVC obtained in dichloromethane-TBAFB [see Fig. 1(a)] and ethanol- $\text{H}_2\text{SO}_4$  [see Fig. 2(b)] media. The use of HCl and acetic acid at different concentrations in ethanol media failed to give conducting PNVC film on the electrode surface.

The suggested mechanism of anodic oxidation of PNVC is the formation of a carbazyl radical cation, which on subsequent dimerization of the 3,6 position gives 3,3'-dicarbazyl, a crosslinked material with electrical-conducting behavior.<sup>21,25,26</sup> As shown in Scheme I, the nonconducting PNVC produced from the monomer can then be oxidized to yield the conducting green polymer.<sup>20</sup>


**Scheme 1.**

The forms obtained by the use of  $\text{HSO}_4^-$  and  $\text{NO}_3^-$  as dopants can be shown as



The conducting form of PNVC can also be synthesized by using white-colored nonconducting PNVC instead of monomer. This prevents possible impurities coming from the monomer.<sup>26,28</sup> To investigate this possibility, dioxane- $\text{H}_2\text{SO}_4$  media in which the nonconducting PNVC is soluble were used, and 0.2 g of nonconducting PNVC was dissolved in 20 mL of dioxane containing 2.0 M  $\text{H}_2\text{SO}_4$  and electrolyzed at 1.0 V. It was observed that a PNVC film, the Raman spectrum of which was similar to that illus-

trated in Figure 2(a), was formed on the electrode surface.

The electrolysis carried out in pure  $\text{H}_2\text{SO}_4$  with no solvent also yielded conducting PNVC film on the electrode surface. Raman spectra for this sample, which contain the basic bands characteristic of the conducting PNVC, are shown in Figure 2(d).

The conductivities of the films obtained by the methods outlined here were not very different from each other, all on the order of  $10^{-6}$  S/cm.

Some of these samples were undoped by keeping them in 2.0 M NaOH for 1 day. The Raman spectra of these undoped samples showed no significant changes compared to those of the conducting forms. The undoped PNVC can be converted into a conducting form when treated with 4.0 M or more concentrated H<sub>2</sub>SO<sub>4</sub>. Redoping is also possible in HNO<sub>3</sub>.

## CONCLUSIONS

Conducting PNVC doped with HSO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> anions can be synthesized electrochemically in dioxane and ethanol. The synthesis of conducting PNVC in media containing HCl or acetic acid was not possible under these experimental conditions. Changing the dopant anion did not cause a significant change in the Raman spectrum of conducting PNVC. Moreover, the Raman spectra of doped and undoped PNVC were not significantly different. Electrochemical synthesis of conducting PNVC films in pure H<sub>2</sub>SO<sub>4</sub> without using a solvent was also found to be possible. Finally, conducting PNVC can be synthesized by the electrolysis of NVC or nonconducting PNVC in dioxane-H<sub>2</sub>SO<sub>4</sub> media.

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