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KINETIC STUDIES IN THE ELECTROINITIATED POLYMERIZATION OF *N*-VINYLCARBAZOLE AND RELATED CONDUCTING POLYMER COMPOSITES

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ABSTRACT

Electrochemical polymerization of *N*-vinylcarbazole (NVC) on platinum electrodes was studied. Effects of concentration, electrode area, polymerization potential, and solvent on the polymerization rate were discussed. Insulating and conducting polymers of NVC can be simultaneously prepared depending on the electrolysis conditions. The insulating PNVC cannot only be converted into a conducting one but can also be blended with other conducting polymers such as polythiophene and polypyrrole. Soluble insulating polymers of NVC were characterized by FTIR, NMR, and DSC studies. Conducting polymers were characterized by FTIR and 4-probe conductivity measurements.

INTRODUCTION

There are few vinyl monomers which polymerize with the facility of *N*-vinylcarbazole (NVC). NVC is a reactive monomer toward radical and cationic polymerization because of its ability to stabilize electron-deficient centers by resonance involving the nonbonding electron pair on the nitrogen atom in the ring. Most of the electroinitiated polymerization studies on NVC have been carried out by controlled-current electrolysis (CCE) [1–3]. Recently a direct electron transfer process in the polymerization of NVC via constant potential electrolysis (CPE) was accomplished in our laboratories [4].

Conducting polymers of NVC [5, 6] as derived by electrochemical means were of much interest after reports on the conducting properties of some compounds such as pyrrole [7]. Poly(*N*-vinylcarbazole), PNVC, which displays interesting electrical properties, has been extensively studied [8–11]. The potentiostatic anodic oxidation of thin coats of PNVC on platinum electrodes, which produces electrically conductive polymers, has been shown to involve crosslinking of the polymer chains through the oxidation of up to 50% of the carbazole moieties in the coat, followed by rapid dimerization of the resulting pendant carbazole cation radicals [12]. The synthesis of composites and copolymers of NVC and pyrrole was described in a recent report [13] where both insulating and conducting polymers of NVC were utilized in the electroinitiated polymerization of pyrrole.

There is an increase in the development of gas sensors for monitoring the composition of gaseous ambients. Several gases have been used via contact with PNVC film to test the gas-sensing ability of conducting polymers including PNVC and its derivatives [14, 15].

In this work the kinetics of nonconducting PNVC polymerization together with blending reactions utilizing pyrrole and thiophene are studied. Some preliminary results in the gas-sensing capability of PNVC are also mentioned.

EXPERIMENTAL

Materials

N-Vinylcarbazole (NVC) was recrystallized from methanol, filtered, dried under vacuum, and stored in the dark. Reagent-grade pyrrole and thiophene were distilled under vacuum and kept in a refrigerator. Tetrabutylammonium fluoroborate (TBAFB) was dried under vacuum and used without further purification. Reagent quality quinone and pyridine were used as purchased as inhibitors to polymerization. The solvents employed were acetonitrile and 1,2-dichloroethane.

Method

Cyclic voltammetry as both a means of measuring the peak potential of monomers and for following the kinetics of polymerization has been reported elsewhere [16]. The kinetic studies were run in CV cells. Aliquots were taken from electrolysis reactions which took place in 1,2-dichloroethane (DCE) and poured into a acetonitrile-TBAFB system in a CV cell. The electrolysis solutions were 0.035 M in NVC. Effects of electrode area, concentration, temperature, and electrode potential were studied. The unreacted monomer concentrations were determined by cyclic voltammetry. Postpolymerization and inhibition studies were carried out via cessation of current and the addition of suitable inhibitors, respectively. The intrinsic viscosities of insulating PNVC were measured in benzene at 25°C. The characterization of insulating PNVC was done by FTIR and NMR spectroscopy and differential scanning calorimetry. The conducting PNVC films were characterized by the aid of FTIR and 4-probe conductivity measurements. The PNVC/Pt electrodes obtained in acetonitrile or DCE were used to electrolyze pyrrole and thiophene in acetonitrile at +1.5 and +1.7 V vs Ag^0/Ag^+ reference electrode, respectively. The concentrations of pyrrole and thiophene were 10^{-1} M and they were added only to the working

electrode side of the electrolysis cell. For the electrochemical polymerization of NVC, a three-electrode system was used. The supporting electrolyte TBAFB, sufficient to make 0.1 M, was placed in the reference arm of the H-cell. Details of the electrolysis system, including the potentiostat and function generator system, were reported earlier [17]. Polymers precipitated either on the electrode (conducting) or in the bulk of the solution (insulating) during the course of reaction were washed with acetone to remove any traces of dimers. The polymers were filtered and dried under vacuum at 30°C for 24 hours.

The gas-sensing properties of the conducting PNVC films were measured against ammonia vapor via a 2-probe.

RESULTS AND DISCUSSION

Cyclic Voltammetry

All the cyclic voltammetry measurements were conducted with the same monomer concentration (10^{-3} M) and supporting electrolyte (TBAFB) (0.1 M). The voltammograms were carried out at room temperature. In all the solvent/electrolyte media there was no reduction peak of the monomer, hence only the oxidation behavior of the monomer is given. The cyclic voltammogram of NVC obtained in the acetonitrile-TBAFB system is given in Fig. 1. The solvent-electrolyte couple was electroinert in the 0 to +3.0 V range vs Ag^0/Ag^+ . NVC has two well-defined irreversible oxidation peaks: +1.25 V and +1.75 V. The anode was coated with a thin green film during CV measurements. As the scan number increases, the peak height decreases due to film formation, but the positions of the oxidation peaks do not change. Along with film formation on the electrode surface, a precipitation in the form of a white polymer in acetonitrile was observed during anodic scanning.

CV of NVC in dichloroethane reveals a broad oxidation peak having a maximum of +1.5 V. The broadness of the peak may well be due to excessive film

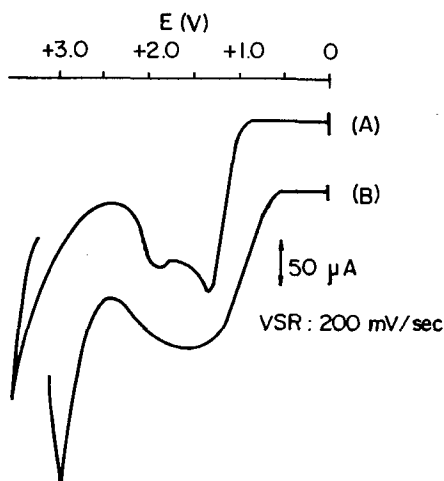


FIG. 1. Cyclic voltammogram of NVC in (A) acetonitrile and (B) DCE.

formation in DCE by a rapid increase in current around +1.2 V which prevents the peak resolution as in the case of acetonitrile.

Controlled Potential Electrolysis

NVC was polymerized via controlled-potential electrolysis (CPE) by applying a potential equivalent to the oxidation potential of the monomer as determined by cyclic voltammetry. Electrolyses were accomplished at room temperature at +1.5 V vs Ag^0/Ag^+ . Concentrations of the monomer and electrolyte were 0.035 and 0.1 M, respectively. The working electrode (anode) area was 1.62 cm^2 . As soon as electrolysis started, a green film appeared on the anode surface and, in addition, a white polymer precipitated in the solution. The color of the solution changed to green or purple during electrolysis. After some time the green film on the anode changed to black. In the literature [18] it is reported that the green color is due to dimer formation.

At the end of electrolysis, the solution in each compartment was transferred into methanol separately in order to achieve the highest yield. The precipitated polymer was powdery and white in color. The polymer film on the anode could not be removed from the surface of the electrode. Therefore, in cases where conducting polymer films were desired, either the electrolysis was conducted overnight or, even better, a small amount of water was added to the system, and this prevented formation of the white polymer, thus enhancing the black film coating on the electrode. This free-standing film can easily be removed from the electrode. The peak potential of NVC in dichloroethane (DCE) was at +1.5 V vs Ag^0/Ag^+ , hence the controlled-potential electrolysis of the monomer was carried out at that potential in order to achieve direct electron transfer from the monomer. The concentration of the monomer was 0.035 M and of TBAFB was 0.1 M. The anode area was the same as in the acetonitrile case. The anode was initially coated with a green film which turned into black. The color of the solution changed to green or purple, but there was no precipitate in the solution. In order to check for the presence of any polymer formation in the solution, the anolyte and catholyte were poured into methanol separately. A white polymer was precipitated from the anolyte as a powder, and there was no precipitation from the catholyte. The film on the anode was thin and could not be peeled off the surface of the electrode. Electrolysis revealed that DCE is a solvent for insulating PNVC while acetonitrile is not.

Kinetic Studies

When the electrolyses were carried out using acetonitrile as the solvent, two products were obtained, one from the anode surface and the other from the solution which precipitated during electrolysis. In the case of dichloroethane, the anode was coated with a film but there was no precipitate in the solution during electrolysis. A white product was obtained when the electrolysis solution was transferred into methanol after the cessation of current.

In order to examine the effect of polymerization potential on the rate of polymerization, the kinetics of polymerization were investigated by applying various potentials. CV of NVC in acetonitrile reveals two oxidation peaks at +1.25 and +1.75 V. Those peak potentials were chosen for the kinetic investigation. In addi-

tion, a potential in between those two peak potentials was chosen (+1.5 V). In the CV, current begins to rise due to oxidation of the monomer at +0.95 V. Therefore, this was yet another potential used to investigate the kinetics of polymerization.

Experiments were performed with 0.035 M NVC, and the area of the working electrode (anode) was 0.16 cm². In the course of electrolyses, definite amounts of polymerization solutions were transferred into acetonitrile-TBAFB solution (CV cell), and the CV of the unreacted monomer was run at various time intervals. The calculated percent conversions are plotted with respect to time in Fig. 2(A). Up to a definite point the percent conversion-time curves rise steadily, after which the increase in percent conversion is more pronounced. In all experiments of the applied polymerization potential, the percent conversion reached the same value, ~75%, and then remained constant. The initial slopes of the curves vary somewhat with the applied potential; however, after ~25% conversion, the rate of polymerization is the same whatever the polymerization potential.

The initial current passing through the electrolysis solutions was found to be dependent on the polymerization potential, as expected. Therefore, the amount of activated monomer decreases as the polymerization potential decreases. Hence, the rate of polymerization was expected to be dependent on the applied polymerization potential. Figure 2(A) confirms this fact up to a point, but thereafter there is no significant change in the rate of polymerization with respect to polymerization potential.

A possible explanation may be as follows: The rate of polymerization has a maximum value at a critical activated monomer concentration. When the polymerization potential is +1.75 V, this critical activated monomer threshold is achieved in a shorter time than other polymerizations performed at lower potentials. As a result, as the polymerization potential decreases, the time required to reach the critical activated monomer concentration increases. Therefore, the initial slopes of the percent conversion-time curves are different with respect to polymerization potential up to a point and then become independent of the potential.

Figure 2(B) represents the effect of electrode area on the rate of polymerization with a monomer concentration of 0.035 M by applying +1.75 V. A large platinum foil with a surface area of 1.62 cm² and a small platinum foil (0.4 cm²) were used as anodes in addition to the wire electrode (0.16 cm²) that was used in experiments described in earlier sections.

Polymerizations conducted by using the platinum electrode wire (0.16 cm²) has shown similar kinetics with the polymerizations in which a small platinum foil (0.4 cm²) was utilized as the anode. The only difference is the time required to reach the maximum rate of polymerization. On the other hand, the S-type behavior of the kinetic curve could not be obtained for polymerizations where the anode was a large platinum foil (1.62 cm²). The critical monomer concentration that was discussed above may be valid for this case also. The critical monomer concentration may be instantly reached after starting the electrolysis because the large surface area of the electrode yields a higher current density, so that a larger amount of monomer can be oxidized in a rather short time. An increase in polymerization temperature enhances the rate of polymerization and the percent conversion as shown in Fig. 2(C). Hence, temperature is an important parameter in the polymerization of NVC in acetonitrile by CPE.

The same experiments were performed by using different concentrations of NVC while keeping the electrode area and the applied potential constant. Figure

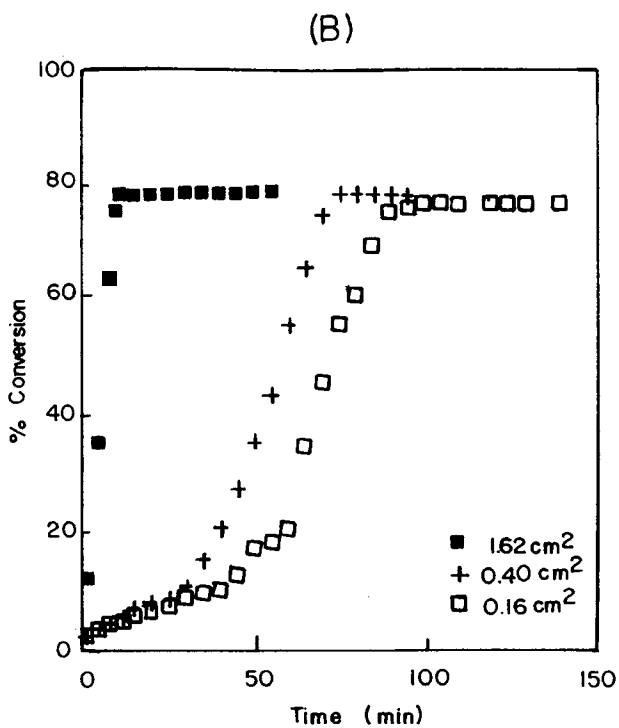
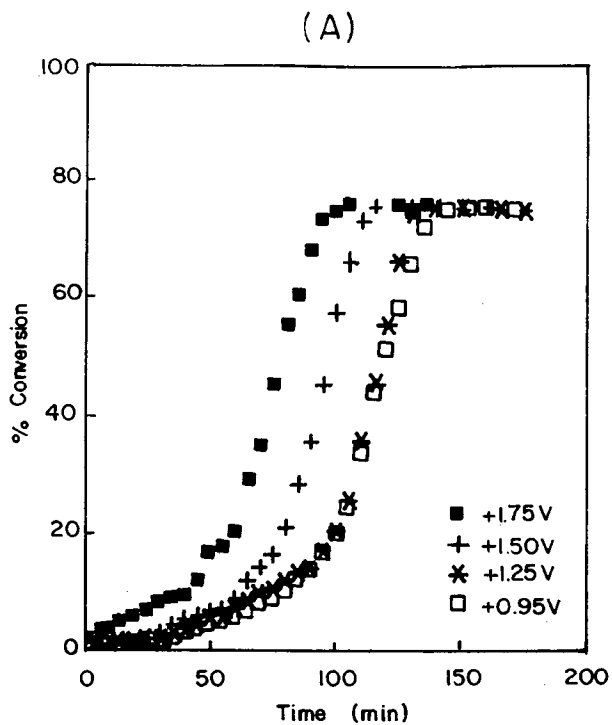
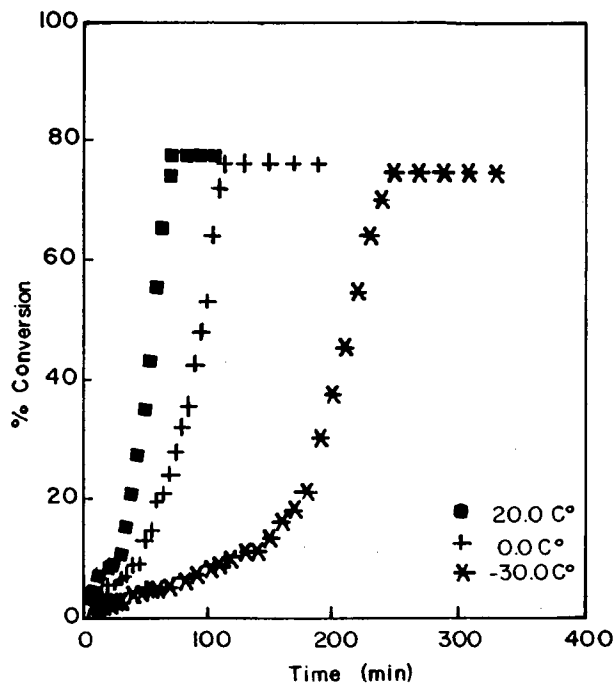
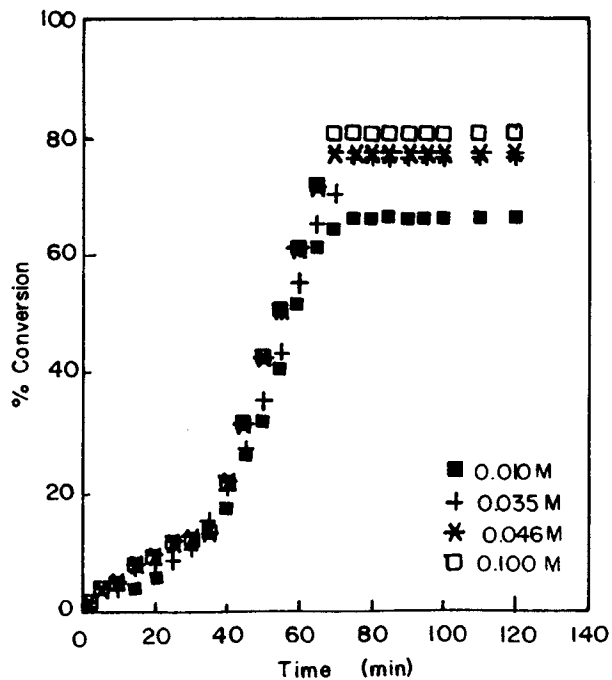


FIG. 2. Effects of (A) polymerization potential, (B) working electrode area, (C) temperature, and (D) concentration on the rate of polymerization in acetonitrile.

(C)



(D)



2(D) presents the kinetic curves. There was no considerable difference in the rate of polymerization even with a tenfold decrease in monomer concentration, excluding the highest achievable percent conversion. This observation satisfies the expectation that with lower monomer concentrations, the time required to reach the equilibrium monomer concentration in polymerization-depolymerization equilibrium is less.

The existence of postpolymerization was checked by electrolyzing NVC in an acetonitrile solution for 45 minutes and then stopping the current. The percent conversion-time plot is presented in Fig. 3. After the current was stopped, NVC continued to polymerize at the same rate as in the presence of current under the same conditions.

The presence of postpolymerization gave the opportunity to check the mechanism of polymerization. Since the electrochemical reaction was oxidation, the active species responsible for polymerization could be cations, the cation radical, or radicals. Therefore quinone was used as a radical inhibitor and pyridine as a cationic inhibitor. The concentrations of the inhibitors were 5×10^{-3} M. Polymerizations were conducted for 45 minutes, then the inhibitors were added one at a time while electrolysis was ceased. It was found that quinone has no effect on the rate of polymerization whereas pyridine prevented further polymerization. So the mechanism of polymerization of NVC in acetonitrile by CPE is cationic in character.

CV of NVC in DCE reveals a broad oxidation peak which has a maximum at +1.5 V. In the first part of the kinetic study, the effect of polymerization potential

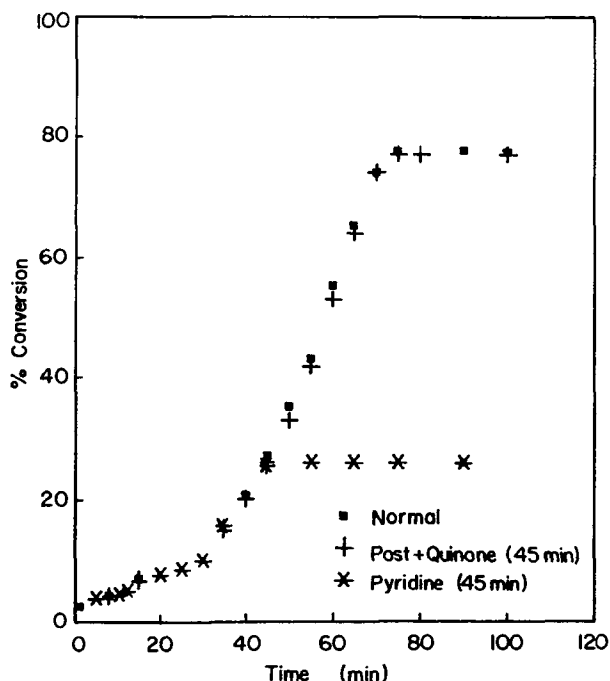


FIG. 3. Effects of postpolymerization and inhibition of 0.035 M NVC in acetonitrile at +1.5 V with a 0.4-cm electrode area.

on rate of polymerization was investigated. +0.95, +1.5, and +1.75 V vs Ag^0/Ag^+ were chosen as the polymerization potentials, the second value being the peak potential of NVC. The results of the experiments and the percent conversion-time plots are given in Fig. 4. The shapes of the kinetic curves were not similar with the S-type curves observed in the case of acetonitrile. Polymerization was slow when the applied potential was +0.95 V. At the higher potentials there was no significant difference in the rate of polymerization with changing polymerization potential. As a generalization, the rate of polymerization increases with increasing polymerization potential after a certain threshold potential.

Figure 4(B) represents the relation between the working electrode area and the rate of polymerization. It is obvious that a larger working electrode area requires a shorter time to reach the maximum percent conversion. The reason is the larger amount of activated monomer with an electrode having a larger surface area.

Electrolyses were also carried out at different temperatures (20, 0.0, -30°C) while keeping the concentration of the monomer and the applied potential constant. Figure 4(C) represents the effect of temperature on the rate of polymerization in DCE, which reveals the same behavior as with acetonitrile. In other words, the rate of polymerization slows down with a decrease in temperature until 20% conversion is reached. After that, there is no significant effect of temperature on the rate of polymerization. This shows the effect of temperature on the initial rate of polymerization rather than the situation as a whole.

The effect of concentration on the rate of polymerization was investigated by using 0.01, 0.035, and 0.1 M monomer concentrations (Fig. 4D). The rates of polymerization were almost the same, excluding the maximum percent conversion points.

Comparison of Figs. 2 and 4 suggests that an accelerating effect of dichloroethane exists. This is especially pronounced with the applied electrolyses potentials, whereas no such conclusion can be deduced by using either different electrode areas or temperatures. We attribute this to the fact that dichloroethane has a chain transfer constant of almost zero in cationic polymerization whereas acetonitrile has a high constant. Since only the monomer consumption was studied in terms of the kinetics of polymerization, this variation in the kinetics of NVC in the two media is quite reasonable.

In the kinetics of postpolymerization, which utilizes the cessation of electrolysis, the change in monomer concentration was also followed by cyclic voltammetry (Fig. 5). It was observed that the reaction continued when electrolysis was stopped at the 7th minute. In order to check the character of the active species responsible for polymerization, quinone and pyridine (both 5×10^{-3} M) were used. We observed that quinone has no effect on the rate of polymerization whereas pyridine inhibits the polymerization of NVC. As a result, the cationic mechanism is also valid here.

Electrochemical polymerization of NVC by CPE using acetonitrile and dichloroethane yields two kinds of polymers. The first one is obtained from the anode surface as a black coating and the second as a white powder which is precipitated in methanol. One of the aims in this work was to obtain conducting PNVC films. Conductivity measurements showed that the white polymer was an insulator while the black polymer has conducting properties. Moreover, the insulating white polymer can be further polymerized into a conducting polymer in dichloroethane me-

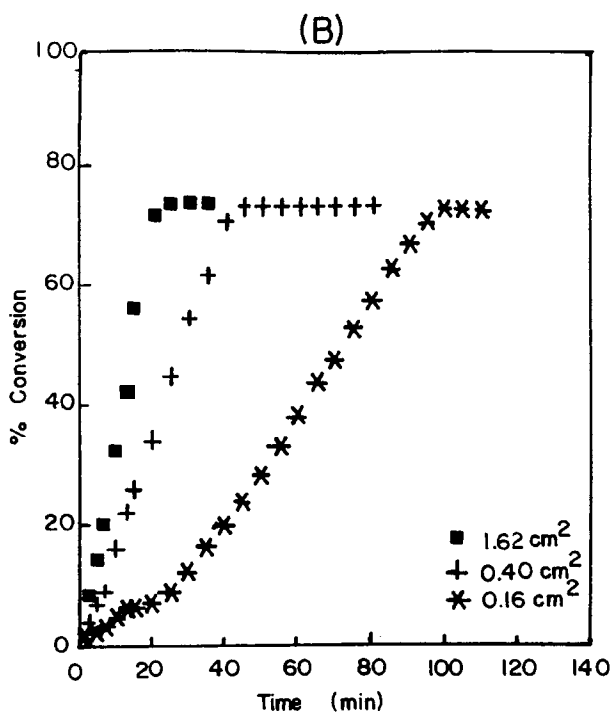
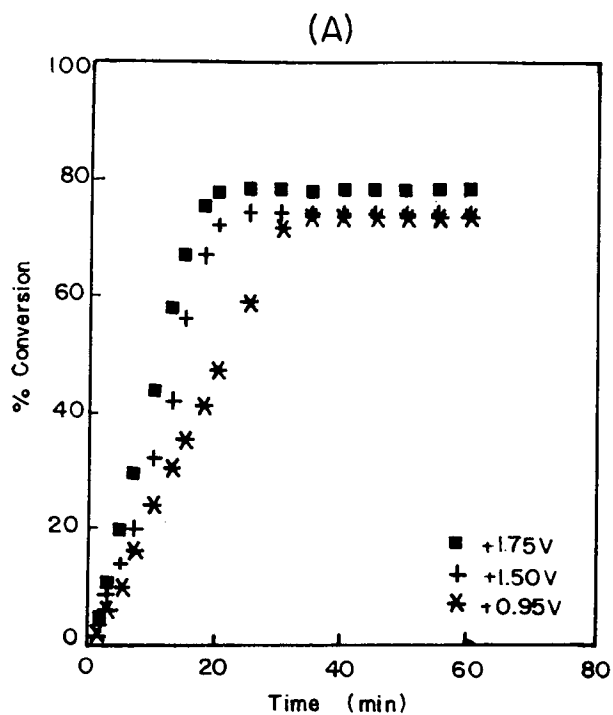
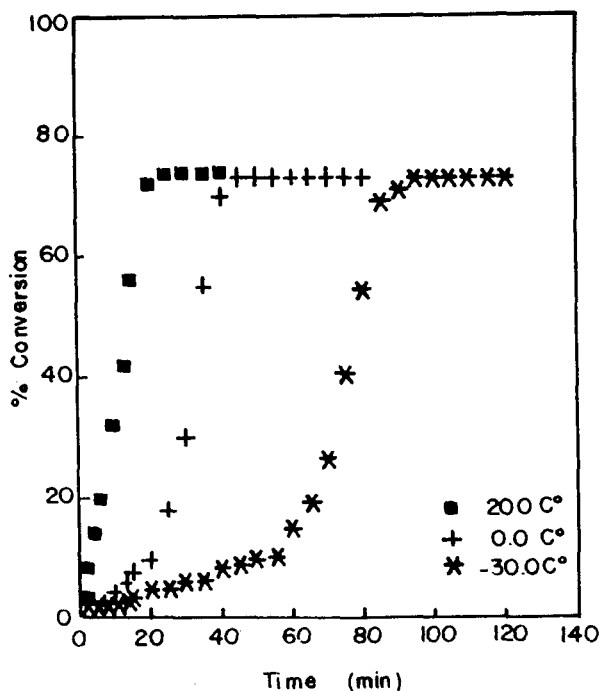
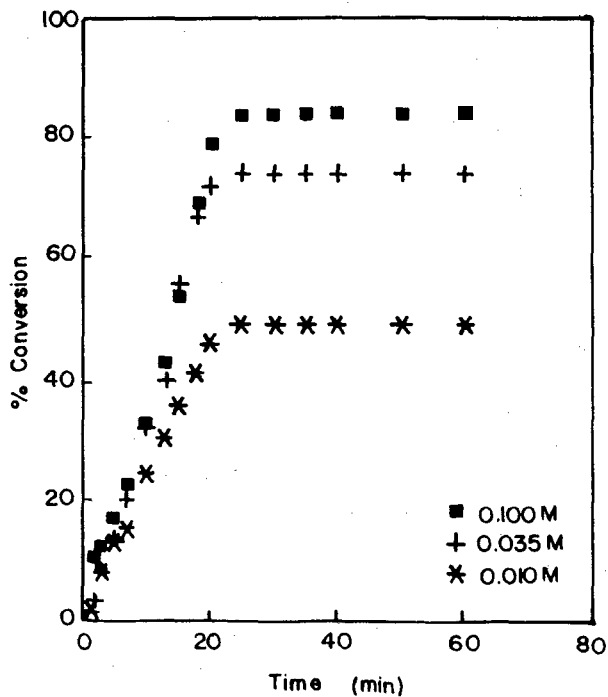


FIG. 4. Effects of (A) polymerization potential, (B) working electrode area, (C) temperature, and (D) concentration on the rate of polymerization in DCE.

(C)



(D)



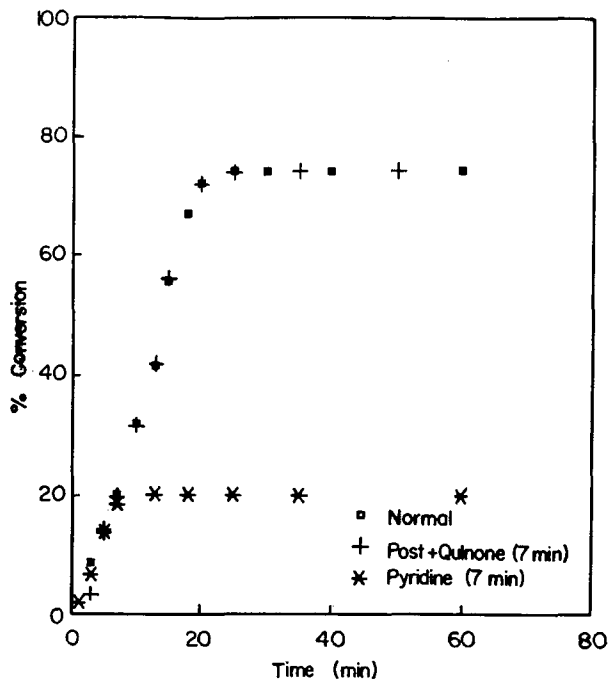


FIG. 5. Effects of postpolymerization and inhibition of 0.035 M NVC in DCE at +1.5 V with a 1.62-cm electrode area.

dium. That is, the polymer which is insoluble in acetonitrile is soluble in DCE and further reaction is possible. An extensive examination on the matter was made previously [19]. We believe the small difference between the conductivities of the polymers synthesized in different media (in favor of DCE) can be explained by the 3 and/or 6 more position linkages in DCE compared to PNVC [19]. However, the conductivity was not very high (i.e., in the region of semiconductors), and therefore we tried to prepare blends with polymers having higher conductivities in order to increase the conducting properties. Polypyrrole and polythiophene were selected for this purpose because both of them are well known conducting polymers. In addition, the synthesis of these conducting polymers into free standing films is achieved by electrochemical polymerization methods, and that fits the method used throughout this work.

Polypyrrole is a conducting polymer with wide applications. It is generally obtained by electrolyzing pyrrole monomer in acetonitrile or water with suitable supporting electrolytes. TBAFB is the most widely used supporting electrolyte when acetonitrile is utilized as the solvent. In this work acetonitrile and TBAFB were chosen as the solvent/supporting electrolyte system for the polymerization of pyrrole. Pyrrole is polymerized by using a PNVC-coated anode electrode. Both acetonitrile and dichloroethane were utilized as polymerization solvents to obtain PNVC-coated electrodes.

Attempts to obtain high quality PNVC conducting films which can be peeled off the electrode surface either by changing the reaction parameters in a kinetic

investigation or by using different solvent systems were unsuccessful. The formation of a white polymer in solution during electrolysis decreases the quality and quantity of the conducting polymer film.

Dubois et al. [5] examined the influence of the same parameters for the formation of thin PNVC films which adhere to the metal. They succeeded in obtaining such films by preventing nonfilm-forming polymerization by the addition of small amounts of water. Therefore, water was added (2×10^{-2} M) to both acetonitrile and dichloroethane in the synthesis of good quality PNVC films.

Polymer blends were prepared by first coating the anode with a PNVC film in a slightly hydrated acetonitrile/TBAFB or dichloroethane/TBAFB system, and then polymerizing pyrrole onto that PNVC/Pt electrode in acetonitrile. In order to compare the conductivities of polymer blends with pure polymers, pure polypyrrole was obtained in the acetonitrile/TBAFB system whereas PNVC was synthesized in slightly hydrated acetonitrile or dichloroethane.

The conductivities of the films were measured by the 4-probe technique, and the results are presented in Table 1.

The conductivity of PNVC film formed in acetonitrile was enhanced approximately a hundredfold by blending with pyrrole. The increase in the conductivity was five orders of magnitude higher when dichloroethane was used as the solvent.

Conducting polythiophene is another well-known heterocyclic aromatic polymer which exhibits a variable conducting behavior depending on the synthesis conditions. Polythiophene displays a little less conductivity compared with polypyrrole. On the other hand, it has better environmental properties than polypyrrole.

Poly(NVC-thiophene) polymer blends were prepared as described for pyrrole. It was found that polythiophene also improves the conductivity of PNVC, as seen in Table 1. The increase in the conductivity of PNVC was a thousandfold when it was prepared in dichloroethane and a hundredfold when it was prepared in acetonitrile. It seems that dichloroethane is a better solvent for obtaining higher conductivities, which may also be deduced from the conductivities of pure PNVC films formed in acetonitrile and dichloroethane. This is said to be due to the fact that dichloroethane acts as a solvent for insulating PNVC. Contrary to pyrrole polymerization, it is necessary to produce PNVC before obtaining conducting PNVC.

TABLE 1. Conductivities of the Films Obtained by Controlled Potential Anodic Oxidation of NVC

Film	Conductivity, ^a S/cm	Conductivity, ^b S/cm
Poly(NVC)	5.3×10^{-4}	3.7×10^{-3}
Poly(pyrrole)	23.0	—
Poly(thiophene)	9.7	—
Poly(NVC-pyrrole)	2.0×10^{-2}	2.1
Poly(NVC-thiophene)	4.0×10^{-2}	8.2×10^{-1}

^aFilm prepared in acetonitrile.

^bFilm prepared in DCE.

TABLE 2. T_g and M_v Values of PNVC Obtained in Various Solvents^a

Polymerization solvent	T_g , °C	M_v
Acetonitrile	221.0	7200
Dichloroethane	230.0	9700

^aAll the experiments were conducted under the same conditions except for the polymerization solvent.

CHARACTERIZATION

Depending on the experimental conditions, the electrolysis of NVC can result in the formation of dark green films, which adhere to the electrode surface, and white polymer, either precipitated from the solution or formed in the solution depending upon the type of polymerization used. Pioneering work in the measurement of conductivities of polymers has shown that the white polymer has no conductivity whereas the dark green polymer films exhibit appreciable room temperature conductivities. Therefore, we classified the products and examined their structures according to their conducting properties.

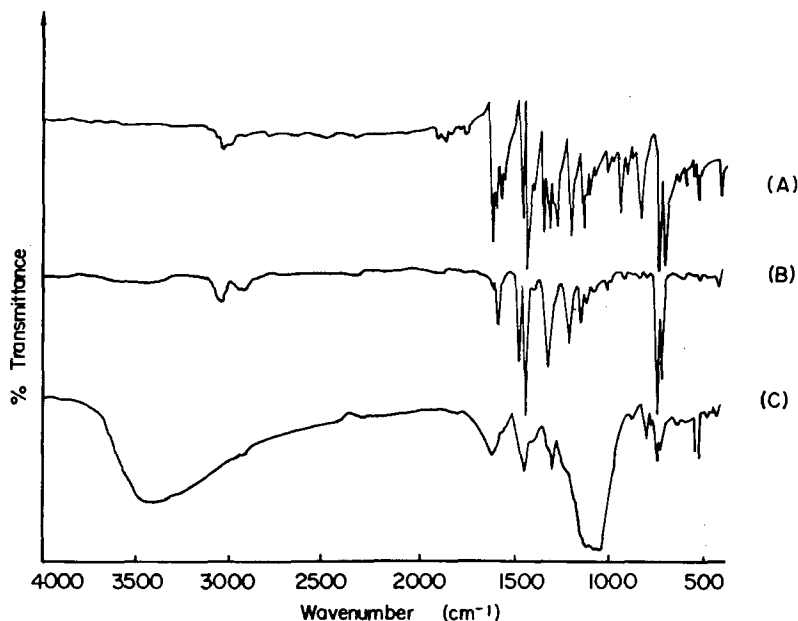


FIG. 6. FTIR spectra of (A) *N*-vinylcarbazole, (B) Poly(*N*-vinylcarbazole), and (C) conducting poly(*N*-vinylcarbazole).

Insulating Polymers

The polymers recovered from the anodic compartment after electrolysis of NVC were white powdery products. They were soluble in organic solvents such as benzene, toluene, THF, and DCE. The softening temperature of the polymers were about 213–230°C. Glass transition temperatures of the polymers obtained in different solvents were between 230 and 214°C, which may be due to changes in molecular weight. These data agree with the literature [3]. See Table 2.

The FTIR spectrum of the white polymer is given in Fig. 6. All the spectra of the samples, regardless of the preparation conditions (different solvents, temperatures, or potentials), are identical. The characteristic FTIR absorption bands at 1638, 963, and 860 cm^{-1} due to the vinyl group of NVC are not present in the spectra of the polymer, indicating that polymerization proceeds via the vinylic group. The FTIR spectrum resembles that of PNVC obtained when HClO_4 is used for polymerization [7].

Regarding the last two Spectra, B and C are similar to the spectrum of the white polymer except for a few peaks. They display additional bands at around 1100 and 880 cm^{-1} ; the former can be ascribed to BF_4^- and the latter to 1,2,4-trisubstituted benzene rings. Yet another absorption band at 800 cm^{-1} is due to the

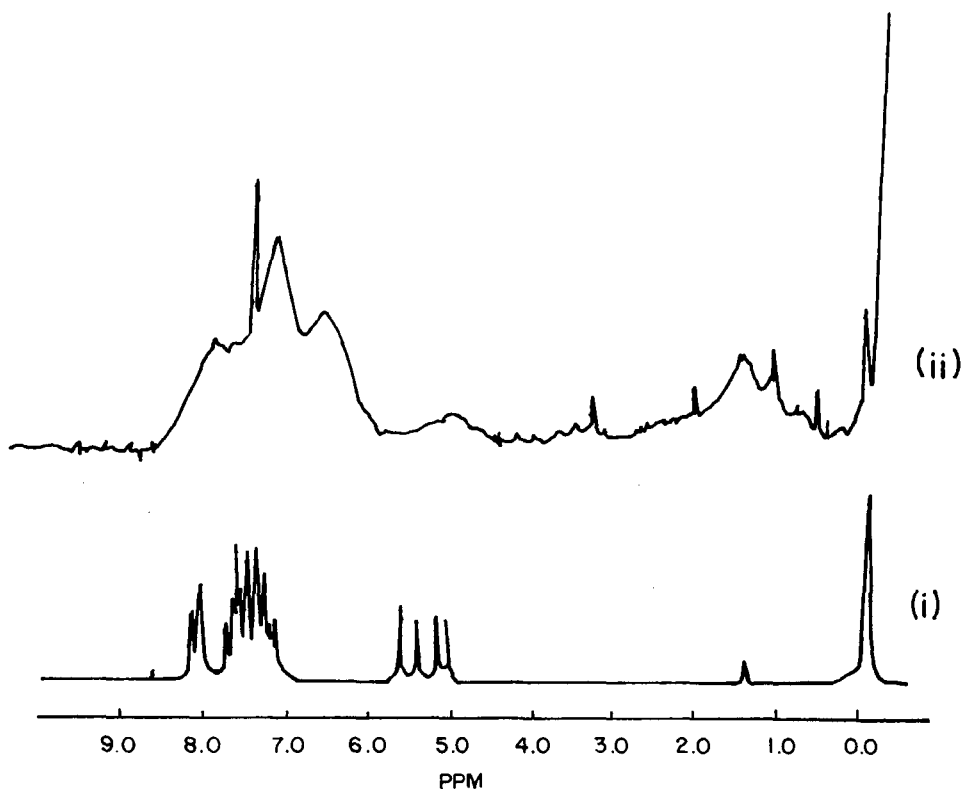


FIG. 7A. ^1H -NMR spectra of (i) *N*-vinylcarbazole and (ii) poly(*N*-vinylcarbazole).

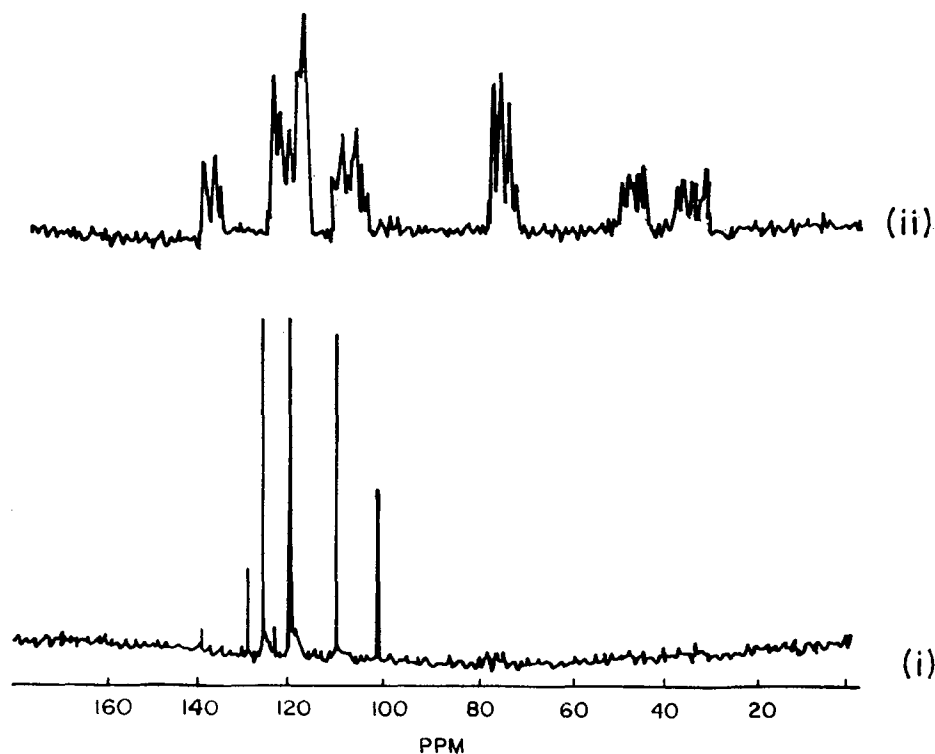


FIG. 7B. ^{13}C -NMR spectra of (i) *N*-vinylcarbazole and (ii) poly(*N*-vinylcarbazole).

C—H out-of-plane deformation vibration of the carbazole ring substituted at the 3-and/or 6-position of the carbazole ring by a coupling reaction of the carbazole cation radical.

The intensity of the band at around 1100 cm^{-1} due to the dopant BF_4^- is an indication of the degree of doping. The highest intensity in this band corresponds to the polymer formed by the electrolysis of NVC in DCE, which also shows the highest conductivity.

Yashimoto et al. [20] reported the assignment of the ^1H -NMR peaks of PNVC synthesized by thermal or cationic polymerization. They assigned a peak at $\delta = 1.5$ ppm to methylene protons, two peaks at 2.7 and 3.6 ppm to the methine proton, a peak at 5.0 ppm to an aromatic proton, and several peaks around 7.0 ppm to the remaining aromatic protons. The 60-MHz ^1H -NMR spectrum of PNVC taken from the anodic compartments after electrolysis of NVC in acetonitrile and solubilized in chloroform- d_3 is given in Fig. 7A. The spectrum is similar to that cited in the literature [5].

Figure 7B shows the ^{13}C -NMR spectrum of PNVC dissolved in CHCl_3-d_3 . The carbon peaks at 35 and 50 ppm were attributed to methylene and methine groups, respectively. The peaks in the 107–142 ppm region were assigned to carbazole groups, while the peaks at 75–78 ppm are due to the solvent, CHCl_3-d_3 .

PNVC films obtained from the electrolysis of NVC in various solvents under different experimental conditions were all insoluble in ordinary solvents. Furthermore, they have shown no glass transition temperatures indicative of excessive crosslinking.

The FTIR spectra of polypyrrole and PNVC obtained in acetonitrile and the PNVC-pyrrole blend are shown in Fig. 8. The conducting polymer blend was prepared by forming a PNVC film on a platinum electrode in acetonitrile and electrocoating it with pyrrole polymerization. The spectra yield the characteristics of both conductive polymers doped with BF_4^- anion.

The conducting polymer blend, where the PNVC film was produced in DCE and then coated by polypyrrole in acetonitrile, has almost the same bands with as the parent polymers. If the ratio of the $1085\text{--}1100\text{ cm}^{-1}$ absorption band is compared for both blends, the degree of doping for the blend obtained in DCE is higher. This is also supported by the conductivity values given in Table 1.

PNVC was prepared as a film on platinum either in acetonitrile or in DCE, and thiophene was coated onto that polymer electrode. Figure 9(B) represents the FTIR spectrum of the former polymer blend and Fig. 9(A) the latter. The same argument discussed above is valid for this case also. If the band at $1085\text{--}1100\text{ cm}^{-1}$ of the blend obtained from acetonitrile is compared with that of the blend obtained from DCE, it is seen that the latter has a higher degree of doping, which is also supported by the difference in conductivities.

GAS-SENSING PROPERTIES OF CONDUCTING POLYMERS

In recent years there has been growing interest in monitoring the composition of gaseous substances. Conducting polymer materials show responses to such gases at ordinary temperatures in contrast to some metal phthalocyanine devices which

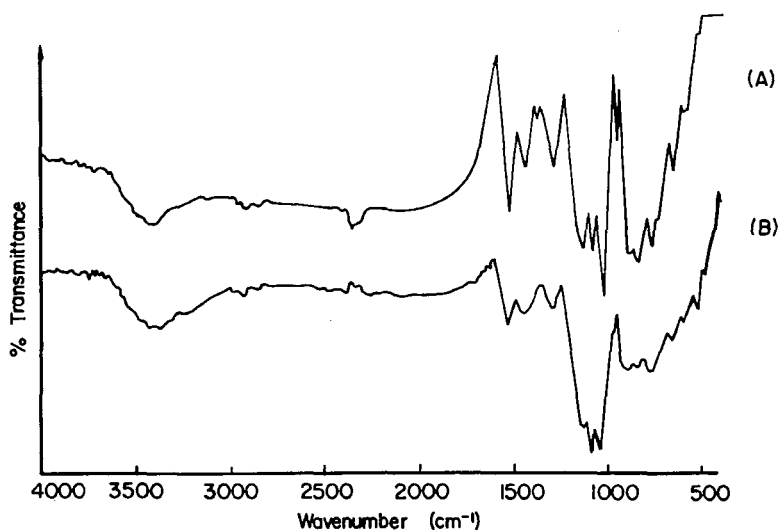


FIG. 8. FTIR spectra of (A) poly(NVC-pyrrole) obtained in DCE and (B) poly(NVC-pyrrole) obtained in acetonitrile.

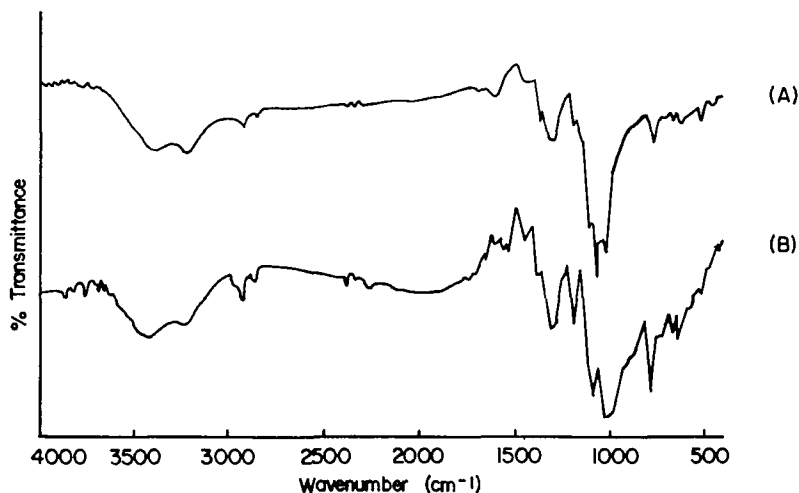


FIG. 9. FTIR spectra of (A) poly(NVC-thiophene) obtained in DCE and (B) poly(NVC-thiophene) obtained in acetonitrile.

TABLE 3. Resistance Change (in kohms) of Several Polymers Prepared in Acetonitrile upon Exposure to NH_3 Vapor (60 second pulses)

	<i>R</i> , kohms	<i>R</i> , kohms ^b
PNVC	126	164
Polypyrrole	0.5	0.83
PNVC/PPy	2.0	3.76
PNVC/PPy ^a	2.0	8.20
PTh	204	1290
PTh/PNVC	300	540
PTh/PNVC ^a	2000	5250

^aPolymerization in dichloroethane.

^bThis column describes the resistance after exposure.

were designed for that purpose but must be operated at 170°C. The gas-sensing properties of polypyrrole were demonstrated by Nylander et al. [21] and those of PNVC by Shirota et al. [15]. Our work with conducting polymers has encouraged us to investigate the gas-sensing responses of the conducting films we synthesized in this work. Ammonia was selected to check the gas-sensing behavior of the films.

Table 3 summarizes the resistance increases after 60 seconds exposure to NH_3 vapor. The apparent discrepancies between Tables 1 and 2 arise from 1) the method of measurement (the latter being via a 2-probe), and 2) different samples. Further studies related to the pulse height and the behavior of blends compared to pure conducting polymers in terms of NH_3 pulses (60 seconds on/60 seconds off) are underway and will be discussed in a future paper.

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REFERENCES

- [1] Y. Kikuchi and H. Fukuda, *Nippon Kagaku Kaishi*, *1*, 200 (1974).
- [2] Y. Kikuchi and T. Uyema, *Ibid.*, *5*, 981 (1974).
- [3] E. B. Mano and B. L. Calafate, *J. Polym. Sci., Polym. Chem. Ed.*, *21*, 829 (1983).
- [4] M. Sacak, B. Hacıoglu, and U. Akbulut, *J. Macromol. Sci.—Chem.*, *A27*,(8), 1041 (1990).
- [5] J. Dubois, A. Desbene-Monvernay, and P. C. Lacaze, *J. Electroanal. Chem.*, *132*, 177 (1982).
- [6] A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, p. 397 (1980).
- [7] J. Bargon, S. Mohmand, and R. J. Waltman, *IBM J. Res. Dev.*, *27*, 331 (1983).
- [8] H. Block, *Adv. Polym. Sci.*, *33*, 93 (1979).
- [9] A. M. Hermann and A. Rembaum, *J. Polym. Sci., Part C*, *32*, 107 (1967).
- [10] H. Hozel, *J. Phys. Chem.*, *69*, 755 (1965).
- [11] H. Block, M. A. Cowd, and S. M. Walker, *Polymer*, *18*, 781 (1977).
- [12] F. J. Davis, H. Block, and R. G. Compton, *J. Chem. Soc., Chem. Commun.*, p. 890 (1984).
- [13] H. Naarman, U.S. Patent 4,468,291 (1983).
- [14] S. Abe, *Chem. Lett.*, *3*, 237 (1977).
- [15] Y. Shirota and H. Hiroshi, *Kobunshi Ronbunshu*, *41*(4), 201 (1984).
- [16] S. Yigit, D. Kusakurek, L. Turker, L. Toppare, and U. Akbulut, *Polymer*, *30*, 348 (1989).
- [17] U. Akbulut, S. Eren, and L. Toppare, *J. Macromol. Sci.—Chem.*, *A21*(3), 335 (1984).
- [18] D. C. Phillips, D. H. Davies, and J. D. B. Smith, *Macromolecules*, *5*, 674 (1972).
- [19] U. Geissler, M. L. Hallensleben, and L. Toppare, *Synth. Met.*, *40*, 239 (1991).
- [20] Y. Yashimoto, Y. Akama, and H. Mikawa, *J. Chem. Soc.*, p. 987 (1969).
- [21] C. Nylander, M. Armgarth, and I. Lundstrom, *Proceedings of an International Meeting on Chemical Sensors*, Fuku Oko, 1983.

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