

# Conducting Polymer Blends of Polypyrrole with Polyvinyl Acetate, Polystyrene, and Polyvinyl Chloride Based Toxic Gas Sensors

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**ABSTRACT:** Blends of the conducting polymer, polypyrrole (PPy), and in the insulating host polymers, polyvinyl acetate (PVAc), polystyrene (PS), and polyvinyl chloride (PVC) resin, have been prepared chemically. Threshold conductivities occur at about 5% for PPy in blends with host polymers. The characterizations of these blends were done by FTIR, UV-visible, differential scanning calorimetric (DSC), scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). The products of the blends have electrical conductivity comparable to PPy and mechanical properties similar to hosting polymers. The response mechanism of the conducting blends to a selection of gases and vapors was investigated using two techniques, measurement of conductance and mass changes using a four-point probe method, and a X-ray fluorescence (XRF) device, respectively. These responses of blends to toxic gases and

vapors are more well explained. Prepared films were exposed to hydrogen halides (HCl, HBr, and HI), hydrogen cyanide, halogens (Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>), monochloroacetic acid (MCAA), 1-3-5 trichloromethyl benzene (TCMB), methylbenzyl bromide (MBB), bromoacetone (BA), and cyanogen bromide (CB). The changes of conductivity of polymers frequently observed are partly due to one stage in the two-stage sorption, perhaps involving the swelling of the polymer, then diffusion gases into polymer chains. The swelling of polymers is a slow process, therefore, preswelled polymer films tend to decrease the response times of blends with respect to gases. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 49–62, 2003

**Key words:** conducting polymer; blend; polypyrrole

## INTRODUCTION

In the last few years, there has been increasing interest in semiconducting polymer films. Most of the work in this area has been concentrated on two main classes of polymers: polyacetylene and its derivatives<sup>1</sup> and polyheterocyclic cations.<sup>2</sup> The interest in polyacetylenes stems from their good mechanical properties, which are associated with high electrical conductivity ( $\sigma$ ) when doped with iodine ( $\sigma = \text{ca. } 10^3 \Omega^{-1} \text{ cm}^{-1}$ ).<sup>3</sup> On the other hand, polyheterocyclic cations such as polypyrrole (PPy) exhibit high stability when exposed to ambient conditions.<sup>4</sup> The drawbacks of these polymers are, for polyacetylene, its poor stability at ambient condition,<sup>5</sup> and for PPy, its poor mechanical properties as indicated by its low elongation at break and its brittleness.<sup>6</sup> These properties severely restrict the technological application of these two classes of polymers.

The preparation of conductive PPy polymer composites or blends are other methods to develop pyr-

role-based conductive materials for commercial applications that possess enough conductivity and satisfactory mechanical properties.<sup>7,8</sup> The chemically prepared PPy was infiltrated on thick porous materials<sup>9</sup> to form composite conductive polymers. Colloidal PPy was also prepared and blended with poly(alkyl methacrylate).<sup>10</sup> In addition, PPy was blended with ionomer gel,<sup>11</sup> poly(vinyl alcohol),<sup>12</sup> and polyamines<sup>13</sup> by using the chemical and electrochemical oxidation routes.

In the preceding work, we reported gas sensing abilities of PPy<sup>14</sup> and polythiophene derivatives.<sup>15,16</sup> We synthesized polyaniline blends and studied their sensing properties by toxic gases and vapors.<sup>17</sup> The produced results were notable. In this article, we present a chemical method for producing flexible, free-standing blend polymer films PPy with polyvinyl acetate (PVAc), polystyrene (PS), and polyvinyl chloride (PVC). These films have good electrical conductivity similar to pure PPy films ( $\sigma = \text{ca. } 1\text{--}40 \Omega^{-1} \text{ cm}^{-1}$  at room temperature), yet they retain the favorable mechanical properties of the host polymers.

We report toxic gas and vapor sensing abilities of PPy blends with conventional polymers such as PVAc, PS, and PVC. The prepared blends have higher thermal stability with respect to PPy, and the PS-PPy

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blend has the highest. The response mechanism of the blends to toxic gases and vapors was investigated using two techniques, measurement of conductance and mass changes using a four-point probe method, and a X-ray fluorescence (XRF) device, respectively.

## EXPERIMENTAL

### Reagents and materials

Pyrrole (Aldrich) was dried with NaOH and fractionally distilled under reduced pressure from sodium or CaH<sub>2</sub>. PVAc, PS, and PVC (medium molecular weight; Aldrich) were used as matrix polymers. Acetonitrile was dried on silica gel and distilled over P<sub>2</sub>O<sub>5</sub> (Merck) in the presence of nitrogen gas. All the other materials and gases used in this work were purchased from Merck and were purified or were prepared by methods found in the literature.

### Instrumentation

Electrical conductivity of the blends was measured by a four probe device (home made) and mass changes were measured with XRF, mode 1, EDXRF 300 link. Elemental analysis was determined with a Perkin-Elmer 2400 CHN. FTIR (8101 M-Shimadzu) was used in spectral studies of the films. Vibrational transition frequencies are reported in wave number (cm<sup>-1</sup>). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), or broad (br). UV-visible spectra were obtained by a Perkin-Elmer Lambda 15 spectrophotometer. Cyclic voltammetry of electrochemical polymerization was carried out using a digital potentiostat DP8 (home made). The thermal properties of the PPy blends were studied by thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) from PL Thermal Science. Scanning electron microscopy (SEM) was employed to study the type of surface morphology of blends. A Cambridge S-360 SEM was used for this purpose.

### Preparation of blends

We prepared a solution of 1 g PVAc, PS, or PVC in 30 mL tetrahydrofuran (THF) in a two-necked, 250 mL round bottomed flask fitted with a dropping funnel under N<sub>2</sub> atmosphere. We inserted a plastic-covered magnetic stirrer follower bar and cooled the flask in an ice bath sited on the stirrer unit. To the cooled and stirred solution we added various amounts of anhydrous ferric chloride. Pyrrole was then added to the stirred solution. The molar ratio of FeCl<sub>3</sub>/pyrrole was chosen to be 2.3:1 and was kept fixed under N<sub>2</sub> atmosphere during our experiments for 1 h, because this led to a high yield, and therefore to high conductivity blends.

A typical procedure can be described as follows: 1 g PVAc, PS, or PVC was dissolved in 30 mL THF and was placed in a two-necked, 250 mL round bottomed flask fitted with a dropping funnel under N<sub>2</sub> atmosphere. A plastic-covered magnetic stirrer follower bar was inserted. Freshly purified pyrrole (0.34 mL, 0.005 mol) was dissolved in 20 mL of THF, added to above solution, and cooled in a dry ice-2-propanol bath. N-Bromosuccinimide (NBS) (0.89 g, 0.005 mol) was added and the mixture swirled for a short time, after removal from the dry ice bath, until all the NBS was in solution. The solution was allowed to stand in a freezer (-10°C) for 2 h during which the solutions became light green. Sodium sulfite (1 g) was added to the solution, and the solvent was concentrated on a rotary evaporator at room temperature.

### Preparation of films

Films (30–60 μm thick) were prepared by casting the blend solutions onto a preheated glass slide, which was then placed in an oven (70°C) with 10 mmHg vacuum condition, after being filtrated with a sintered glass filter. The black solid films thus obtained were washed with a sufficient amount of 10% HCl in water followed by distilled water. Further, the remaining THF and water were removed by evaporation under vacuum at room temperature.

### Toxic gas-vapor generation apparatus

The test gases and vapors were introduced into the sensors with the argon carrier gas in a double impinge exposure cell, with the design consisting of a series of needle valves controlling the gas flow rates, and the other parts of the apparatus described previously.<sup>14,16</sup>

### Cyclic voltammetry

All the cyclic voltammetry of PPy of blends was performed using a conventional three electrode system with a SCE reference, platinum wire counter electrode, and GC disk working electrode. The solution of cyclic voltammetry was 0.1M tetrabutylammonium hexafluoroborate (TBAHFB) in acetonitrile. Blends were deposited on GC disk electrode by casting method. The thickness of the film was about 10–50 μm as determined by SEM.

### Experimental procedure

Before each experiment, samples were swelled by suitable reagents such as diluted basic and acid solutions or volatile organic solutions and then they were heated at 70°C in a 5 mm Hg vacuum to evaporate the residual solvents and humidity out of the polymer films, which could modify the mass and electrical

measurements. However, results would not change much in the absence of preswelling,<sup>14</sup> because these blends have good penetrability to gases and vapors. Then the sample's temperature was regulated at 20°C and a constant gas flow of pure argon was established (100 mL min<sup>-1</sup>) through the cell. All samples were exposed to Ar atmosphere (200–2000 ppm) when they were transferred from the preparation to the measurement equipment. Vapors and gases were sufficiently dry (moisture  $\leq$  0.6 ppm) to facilitate dry experiments on samples. Curves of low concentration of samples during conductivity measurements were produced by allowing a stream of Ar gas, into which gas samples were injected to pass over the blended film. The amounts of gases and vapors were regulated by a magnetic valve and a high-precision flow regulator. Mass and conductivity were measured using XRF and four-probe technique, respectively. The films exposed to gases and vapors were still under the probes.

### Conductivity measurements

For measuring the conductivity of blends, the films or powders were first molded into a disk (about 0.2 cm thick) at an applied pressure of about 4–6 ton/m<sup>2</sup>. The standard four-point method was employed to measure the conductivity of PPy and its blends at room temperature. The average value of four different measurements is given in this article.

## RESULTS AND DISCUSSION

### UV-visible spectroscopy

The UV-visible spectra of polymers were recorded and the produced results are the same as in the preceding work.<sup>17</sup> In the neutral state, polymers showed a maximum of absorption at 300 to 500 nm that could be related to a quite highly conjugated backbone. In the doped state, polymers exhibited a maximum of absorption at 700 to 900 nm that could be related to a high level of doping. The 300 and over 800 nm bands corresponded to the transitions of the valence band to the antibipolaron band and the valence band to the bipolaron band, respectively. A change in the peak position for the valence band to antibipolaron band and valence band to bipolaron band after contact with the dopant agents such as acidic or basic solutions,

active of gases and vapors of the polymer was observed. If the neutral state of polymers is increased, the absorption peaks at 300 to 500 nm will increase and the absorption peaks at 700 to 900 nm will decrease. If the doped state of polymers is increased, the absorption peaks at 700 to 900 nm will increase and the absorption peaks at 300 to 500 nm will decrease.

### FTIR characterization of blends

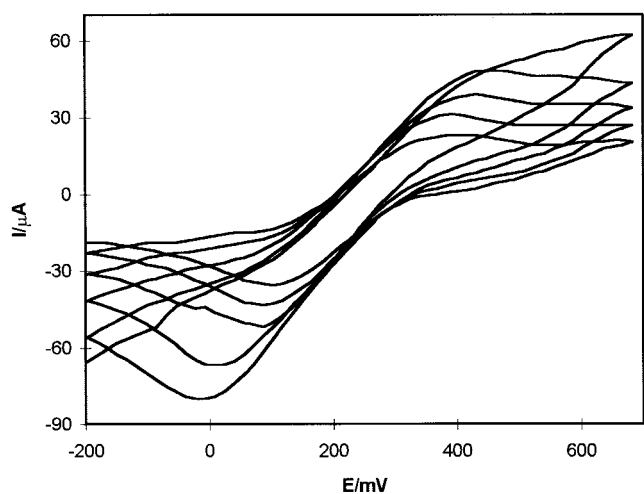
Because the host polymer (PVAc, PS, or PVC) is distributed in the blend, some physical and chemical interactions should occur between PPy and the polymers. FTIR experiments were performed to study these interactions. FTIR (film) and ATR spectroscopic studies on the blends were prepared, and with the reference PPy they are summarized in Table I, where FTIR spectra of three samples are compared. All spectra show a sharp band at 3400–3460 (br) cm<sup>-1</sup> (N—H stretching), 3010–3160 (sh) cm<sup>-1</sup> (C—H stretching aliphatic), and 2960–2995 (sh to m) cm<sup>-1</sup> (C—H stretching aromatic), and the region below 1800 cm<sup>-1</sup> contains bands at 1540–1555 (m) cm<sup>-1</sup> (special stretching mode), 1310–1370 (w), 1100–1200 (m) cm<sup>-1</sup> (N—H plane mode), 1050 (m), and 920 (s) cm<sup>-1</sup>, which are characteristic for the pyrrole moiety.<sup>18</sup> The FTIR spectra of the blends in the region below 1800 cm<sup>-1</sup> are identical to that of PPy. For PPy/PVAc, PS, or PVC blends absorptions at the 2960–2995 cm<sup>-1</sup> regions corresponding to the C—H stretching vibrations are seen, but they are weak. The bands at 1085–1100 (m to s) cm<sup>-1</sup> regions are seen for all samples that correspond to symmetric C—H in plane mode. One can therefore conclude that there is not strong chemical bonding between PPy and host polymers. PPy appears to be only mechanically blended with PVAc, PS, or PVC. However, some hydrogen bonding may exist between these.

### Electrochemical studies

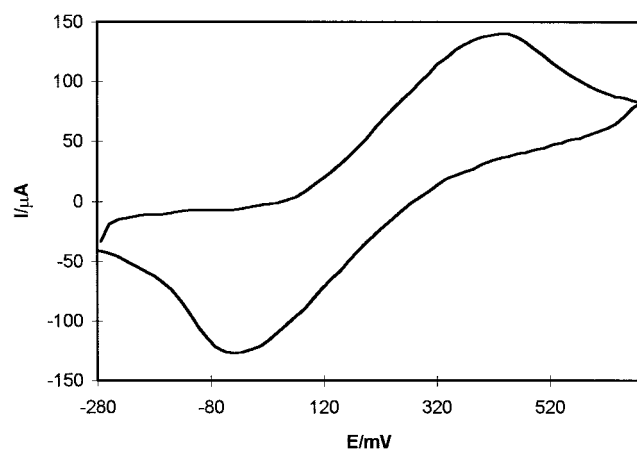
The electrochemical behavior of these blends in 0.1M TBAHFB in acetonitrile, investigated by cyclic voltammetry, is shown in Figure 1. The PPy blends have good electrochemical behavior on the GC disk electrode surface versus SCE. Table II shows the oxida-

TABLE I  
FTIR Spectra Data of PVAc-PPy, PS-PPy, PVC-PPy blends (Film)

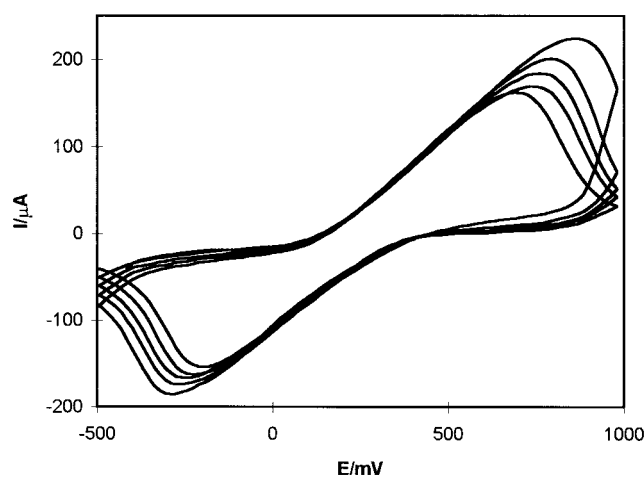
Blend	Wave number
PPy	3390(w), 1520(sh), 1450(sh), 1350(sh), 1200(sh), 1000(sh), 980(sh)
PVAc-PPy	3420(br), 3012(w), 2990(sh), 11710(s), 1600(sh), 1555(m), 1420(s), 1370(w), 1100(m), 1053(m), 925(s)
PS-PPy	3460(m), 3050(w), 2965(sh), 1660(s), 1610(s), 1550(m), 1450(w), 1410(m), 1320(w), 1115(m), 1050(m), 930(s)
PVC-PPy	3450(br), 3055(w), 2970(m), 1510(m), 1545(m), 1410(m), 1330(w), 1200(m), 1051(m), 920(s)



(a)



(b)



(c)

**Figure 1** Cyclic voltammograms of (a) PVAc-PPy, (b) PS-PPy, and (c) PVC-PPy (70/30 w/w) blends, 0.1M TBAHFB in acetonitrile, GC disk electrode versus SCE, scan rate = 50 mV/s.

**TABLE II**  
Oxidation and Reduction Potentials of Blends (mV)

Sample	Oxidation	Reduction
Blend (PVAc-PPy)	375	100
Blend (PS-PPy)	420	-20
Blend (PVC-PPy)	700	-210

tion-reduction potential of blends obtained on electrode surface.

### Measurement of PPy percentage in blends

We used elemental analysis to assess the percentage of involved polymers in the produced mixture. Assessing the percentage of the mixture is important because in this way we are able to analyze the quantity and quality of electron conductivity in the mixtures. In all the mixtures, we will make changes in factors such as: density of oxidant, solvent, density of monomers, and changes in polymer. Because we intended to get the acceptable condition in order to use in sensitivity usage. For this reason we studied elemental analysis on reliable films in view of electrical conductivity, stability, and mechanical properties. Because provided polymer bases on PPy and on the other hands, hosting polymers are without nitrogen atom, so by measuring the percentage of nitrogen in elemental analysis we can achieve the percentage of PPy in blends. We used the following equation for calculating the PPy percentage in blends. To begin with, we measured percentage of theoretical mass of nitrogen in each monomer unit or base hosting polymers with pyrrole:

Percentage of theoretical mass of nitrogen in blends

$$= \frac{\text{Molecular mass of nitrogen}}{\text{Mass unit of monomer (hosting polymer units with pyrrole)}} \times 100 \quad (1)$$

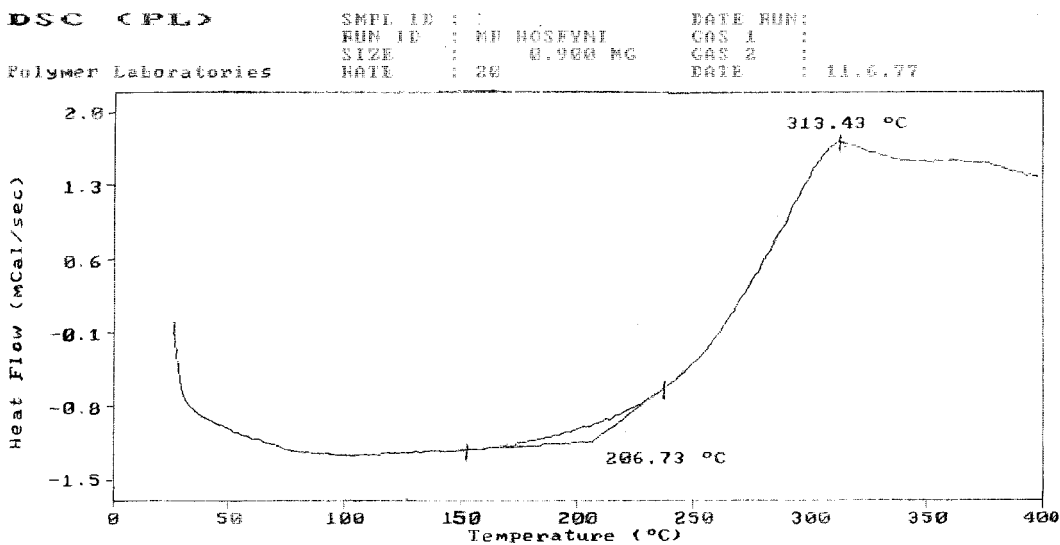
Percentage of polypyrrole (%PPy)

$$= \frac{\%N \text{ Found}}{\text{Theoretical mass of nitrogen in blends}} \times 100$$

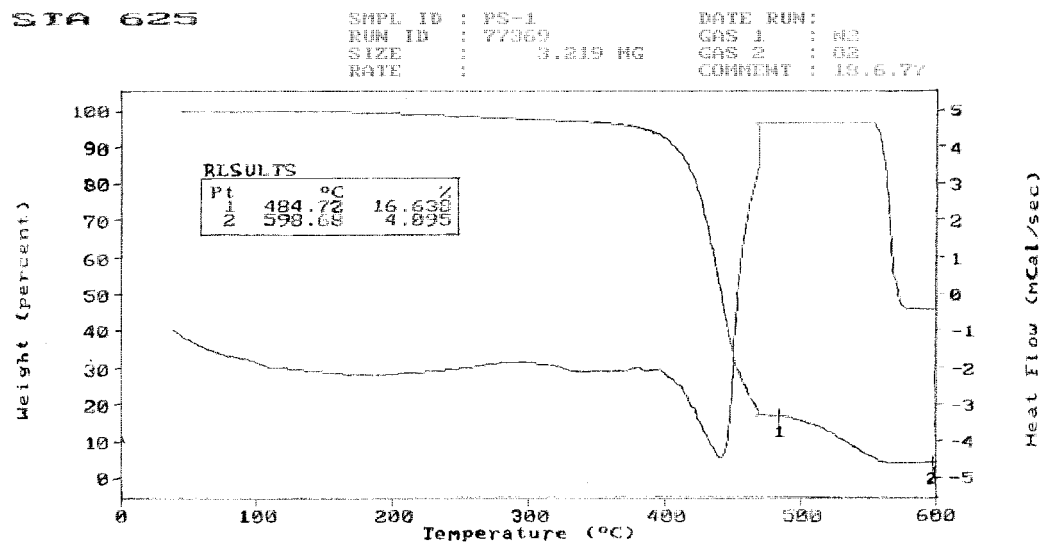
The produced nitrogen percentage by elemental analysis and percentage of PPy in blends is shown in Table III.

**TABLE III**  
Elemental Analysis

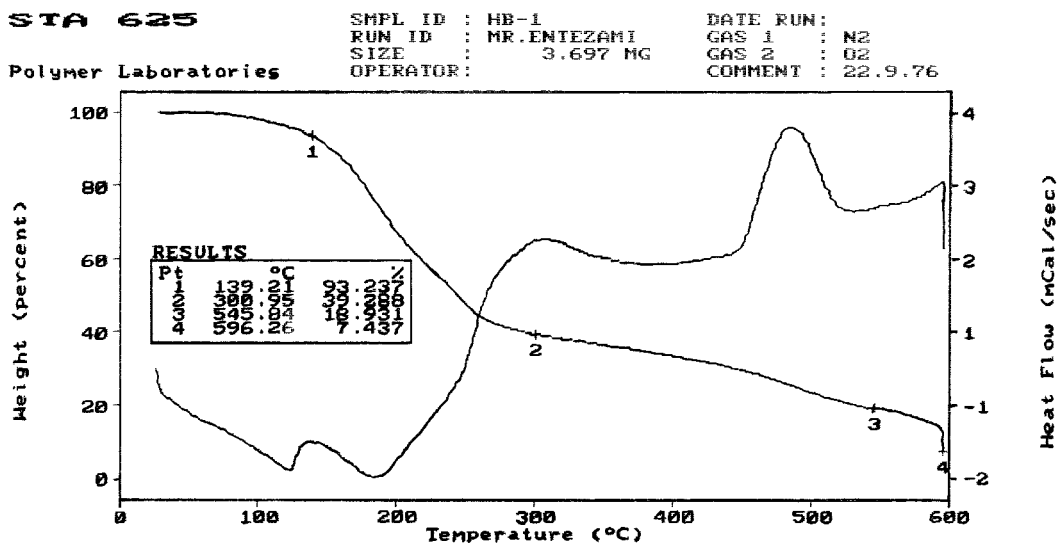
Blend	%N	%PPy
PVAc-PPy	5.6	26.8
PS-PPy	7.3	34.95
PVC-PPy	7	33.5



(a)



(b)



(c)

Figure 2 STA (DSC and TGA) thermograms of (a) PVAc-PPy, (b) PS-PPy, and (c) PVC-PPy (70/30 w/w) blends.

**TABLE IV**  
Thermal Analysis Data

Blend	TDT (°C) <sup>a</sup>	PDT (°C) <sup>b</sup>	PDT (°C) <sub>max</sub> <sup>c</sup>	$\gamma_c$ (%) <sup>d</sup>
PVAc-PPy	120	160	206	4.14
PS-PPy	400	440	484	4.09
PVC-PPy	100	130	316	2.69

<sup>a</sup> Initial decomposition temperature.

<sup>b</sup> Polymer decomposition temperature.

<sup>c</sup> Maximum polymer decomposition temperature.

<sup>d</sup> Char yield at 600 °C.

### Thermal properties

The most important and yet least reliable factor in the study of heat stable polymers is the measurement of thermal stability. Thermal properties of polymers were investigated by TGA and DSC. A representative TGA and DSC curve is shown in Figure 2 and the results are summarized in Table IV. The methods of interpreting TGA results are numerous and also lack standardization. Some of these note the temperature of the 5–10% loss, or by the temperature inflection of the downward slope, or by the first detectable break in the curve. The initial decomposition temperature (IDT), the temperature at 10% weight loss (PDT), and the maximum polymer decomposition temperature (PDT<sub>max</sub>) ranged from 300–400°C, 400–485°C, and 200–300°C for PVAc-PPy, PS-PPy, and PVC-PPy blends, respectively. The residual weights ( $\gamma_c$ ) of the polymers were reported at 600°C. These polymers were stable in N<sub>2</sub> atmosphere up to presented temperatures.

### SEM

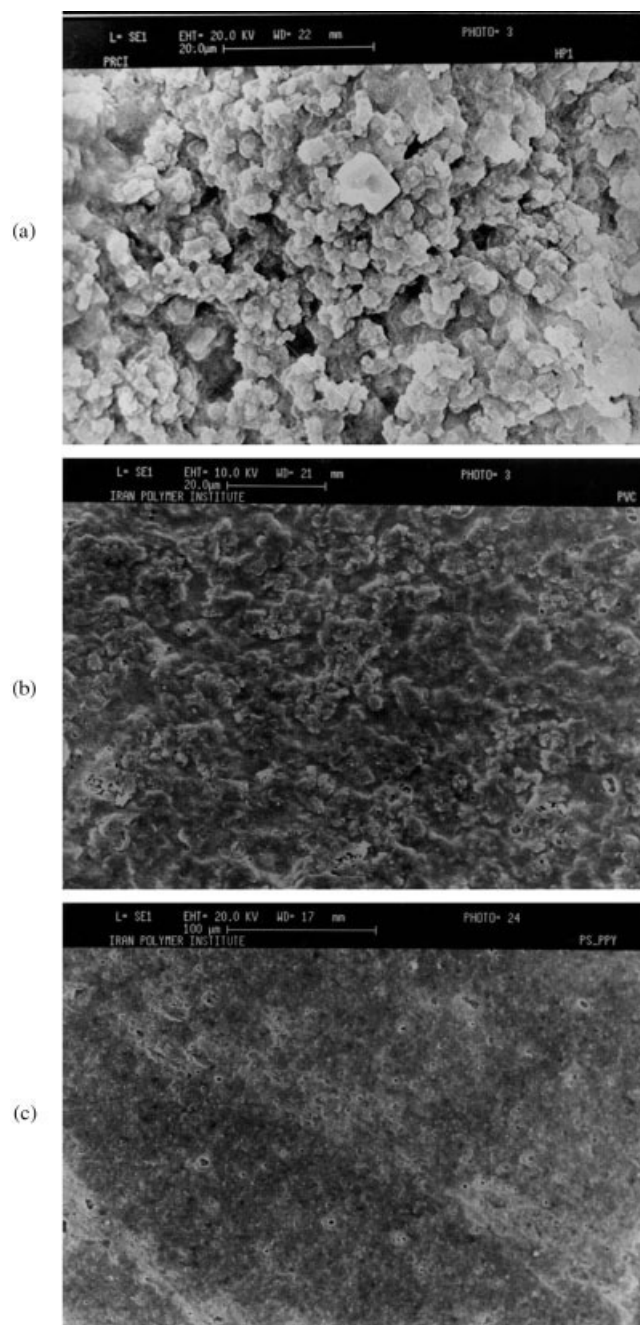
For studying the morphology and the external form of a material, SEM can be used. Scanning electron micrographs for the PPy, PVAc-PPy, and PS-PPy blends containing 30 wt % PPy are presented in Figure 3. Morphologies based on aggregated particles were observed for the samples prepared. In these films, the primary particles are distributed in a completely homogenous phase. A distinct PPy phase could be detected by SEM and blending processes were accomplished successfully. Dramatic changes in morphologies occurred in the films prepared by exposure to gases and vapors before 1 h. Figure 4 shows the SEM micrograph of the PVC-PPy blend before and after a 1 h effect on the TCMB gas. The SEM pictures show that the surface of the blend was apparently swelled and degraded after 1 h effected TCMB vapors.

Table V shows the effect of the mole ratio of oxidant (ferric chloride) to pyrrole on the conductivity. There is an optimum mole ratio of oxidant to pyrrole in the range of 2.3:1. The conductivity of the blend increases rapidly with increasing amounts of oxidant below the optimum value, and decreases with a further increase

in the oxidant mole ratio. As expected, the yield of the blend increased with increasing oxidant concentration. The decrease of the conductivity beyond the maximum is probably due to the decrease in the average degree of polymerization. This implies shorter conjugation lengths.

### Stability of blends

Although PPy is more stable than other conductive polymers to the action of the environment, its conduc-



**Figure 3** SEM micrographs of (a) PPy, (b) PVAc-PPy, and (c) PS-PPy blends.

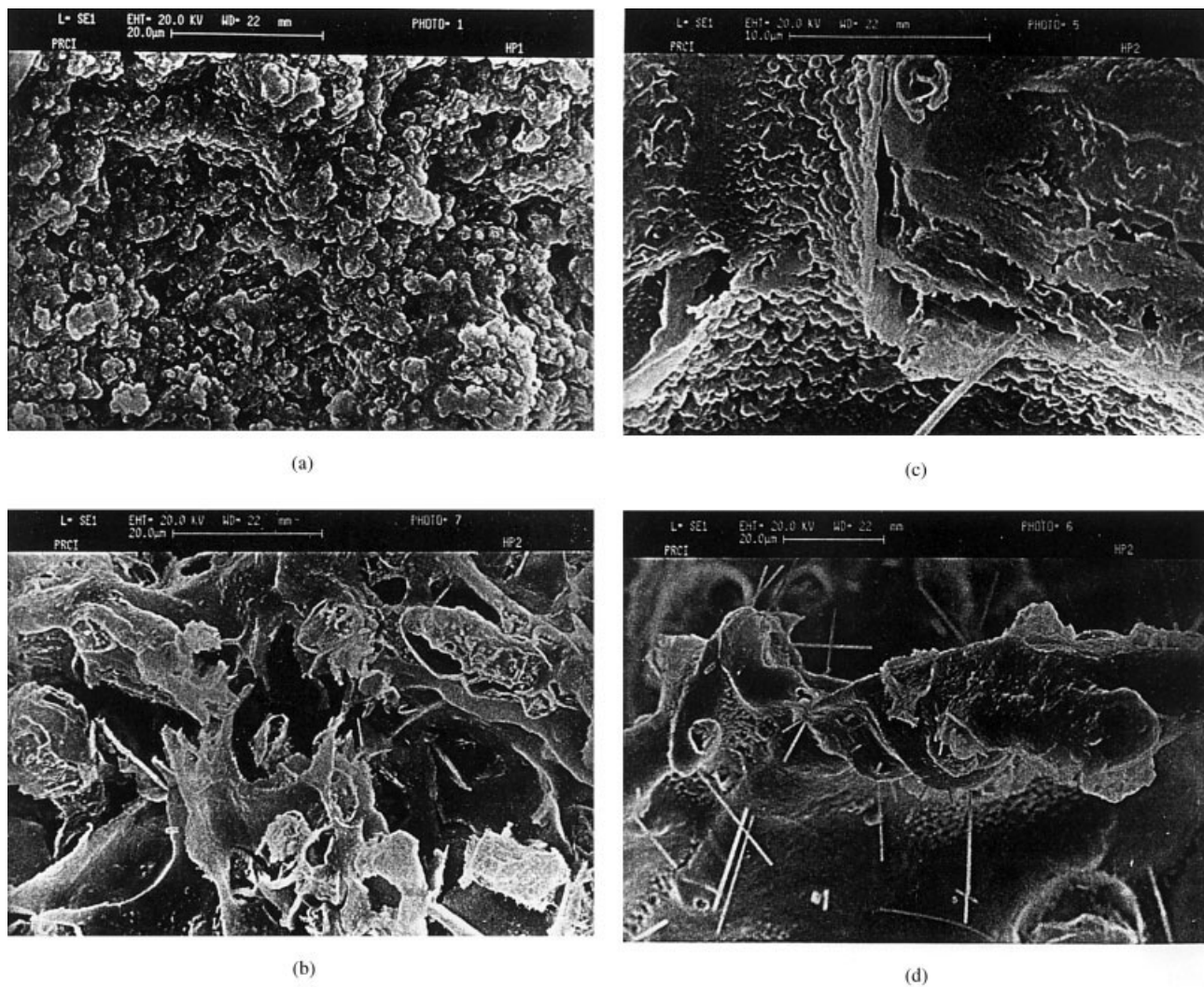


Figure 4 SEM micrographs of PVC-PPy blend (a) initial state, (b) swelled state, (c,d) after 30 minute exposure to TCMB gas.

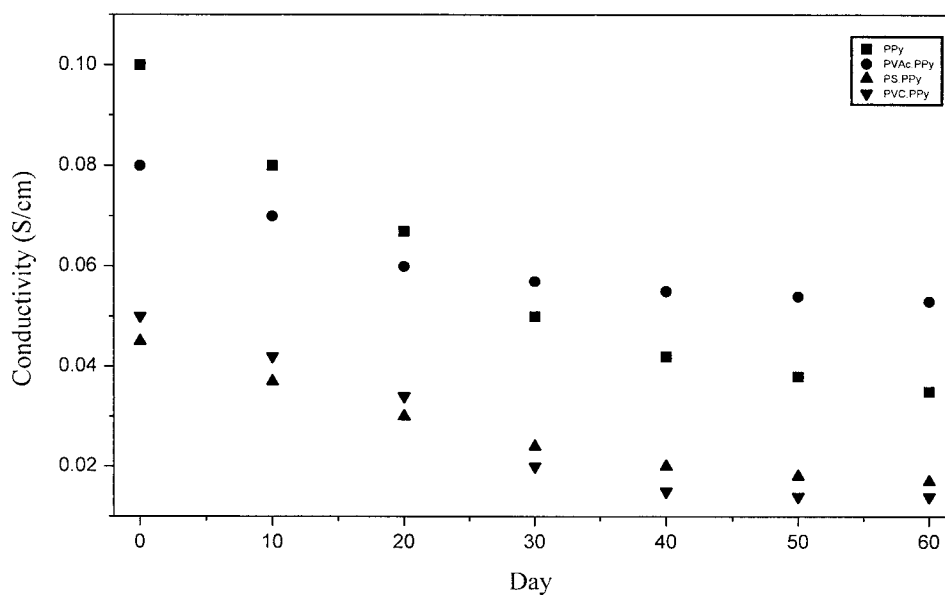


Figure 5 Conductivity of PPy, PVAc-PPy, PS-PPy, and PVC-PPy blends against storage time.

TABLE V  
Effect of the Molar Ratio of FeCl<sub>3</sub>/Py on the Conductivity (S/cm) and Properties of the Films in THF Solvent

Molar ratio of FeCl <sub>3</sub> /Py	Conductivity of blends			Remarks on the films
	PVAc <sup>a</sup> -PPy	PS <sup>b</sup> -PPy	PVC <sup>c</sup> -PPy	
1/1	$3.1 \times 10^{-3}$	$8.9 \times 10^{-2}$	$6.6 \times 10^{-3}$	Smooth, flexible, most strong
2/1	$7.8 \times 10^{-3}$	$4.5 \times 10^{-3}$	0.019	Smooth, flexible, strong
3/1	$7.1 \times 10^{-4}$	$8.3 \times 10^{-4}$	$2.1 \times 10^{-3}$	Smooth, slightly brittle, strong
1/2	$9.2 \times 10^{-4}$	$1.2 \times 10^{-3}$	$7.3 \times 10^{-3}$	Less smooth, slightly brittle, strong
1/3	$4.2 \times 10^{-3}$	$3.6 \times 10^{-3}$	0.01	Less smooth, brittle, strong

<sup>a</sup> Synthetic polymer.

<sup>b</sup> Containing 5% wt polybutadiene.

<sup>c</sup> Containing 1–2% wt DOP (di-octylphthalate).

tivity still decreases during its exposure to the environment. Figure 5 presents the conductivity of PPy and its blends against the exposure time. The PPy prepared here has lost almost 50% of its conductivity after 45 days of exposure to the atmosphere. On the other hand, the PPy/PVAc, PS, and PVC blends remained more stable and the PS-PPy blend was most stable. The blend polymers have higher stability in the environment than the pure PPy, because the insulators (PVAc, PS, and PVC) not only provide mechanical strength but also prevent the exposure of PPy to the atmosphere. The PPy curve does not show this in the figure.

#### Mass and conductivity measurements for sensing of toxic gases and vapors

The results of XRF measurements of PPy blends are reported in Tables VI–VIII. When the concentration of test samples increased, the concentrations of Cl<sub>2</sub> and Br<sub>2</sub> increased. Tables IX–XI show the conductance measurements of PPy blends that were affected by different concentrations of toxic gases and vapors. The conductivity of PPy blends increased upon exposure

to tested samples. The conductivity changes upon exposure to these relatively small gas and vapor concentrations were almost reversible. When higher concentrations of samples were used, the conductivity changes become smaller and partly irreversible. The results in the tables show that the tested samples had exposure to the produced halogens after 60 min and to other gases and vapors after 20 min.

The absorption of gases and vapors into polymer film appears to be a two stage process involving firstly the penetration of vapors into the polymer accompanied by swelling and then diffusion at an increased rate into the swollen rubbery material. Full recovery is not attained after the first exposure leading to a second exposure with a modified polymer containing initial concentrations of gas and vapor. Swelling is the rate determining step of the sorption.

The investigation of conductivity and stability of doped blend films showed significant changes in conductivity when the polymers were affected with hydrogen halides, hydrogen cyanide, halogens, and halomethyl compounds. It showed that the diffusion of halogens into polymer chains is a slow process,

TABLE VI  
Mass Changes Determined by XRF Method for Blend PVAc-PPy

Rel. concentration (ppm)	200	500	800
Cl <sub>2</sub>	1.9	4.2	5.5
Br <sub>2</sub>	3.5	7.1	8.3
I <sub>2</sub>	7.9	13.3	20
HCl	1.8	4.6	5.1
HBr	4.0	6.3	10.1
HI	7.6	9.0	16.3
MCAA	0.4	0.8	1.9
TCMB	2.5	7.3	11.3
BA	2.1	3.6	7.6
CB	4.6	5.9	8.3
MBB	2.6	5.6	9.1

Mass Changes are measured by relative percentage halogen.

Blend (PVAc-PPy) for concentration of samples; X-ray, 0–20 KeV; intensity, 2000–6000 cts.

TABLE VII  
Mass Changes Determined by XRF Method for Blend PS-PPy

Rel. concentration (ppm)	200	500	800
Cl <sub>2</sub>	1.3	3.6	5.4
Br <sub>2</sub>	3.1	6.7	8.0
I <sub>2</sub>	7.2	12.9	19.2
HCl	1.6	4.3	4.8
HBr	3.9	6.1	9.9
HI	7.6	8.8	15.4
MCAA	0.39	0.75	2.0
TCMB	2.4	7.1	11.1
BA	2.3	3.3	7.4
CB	4.3	5.6	8.1
MBB	2.3	5.2	8.7

Mass changes are measured by relative percentage halogen.

Blend (PS-PPy) for concentration of samples; X-ray, 0–20 KeV; intensity, 2000–6000 cts.



**TABLE VIII**  
Mass Changes Determined by XRF Method for Blend PVC-PPy

Rel. concentration (ppm)	200	500	800
Cl <sub>2</sub>	2.1	4.3	6.4
Br <sub>2</sub>	3.6	7.2	8.9
I <sub>2</sub>	8.0	14.4	24
HCl	2.4	5.5	6.2
HBr	4.4	6.1	11.1
HI	8.0	10.2	17.9
MCAA	0.4	1.0	1.9
TCMB	2.8	7.7	11.4
BA	2.1	4.3	7.8
CB	4.9	6.5	8.1

Mass changes are measured by relative percentage halogen.

Blend (PVC-PPy) for concentration of samples; X-ray, 0–20 KeV; intensity, 2000–6000 cts

probably because they are molecular species. The stability of doped films with hydrogen halides, hydrogen cyanide, halogens, and halomethyl compounds was from a few weeks to several months. The results of XRF and conductance polymer's exposure toxic gases and vapors showed that conductivity and absorption are increased with increasing the concentration of the samples. The halomethyl compounds show better conductivity than similar compounds, because the rate of molecular diffusion and doping process are increased by released Cl<sup>·</sup> and Br<sup>·</sup> radicals (Tables IX–XI).

### Response times

Reducing response times of conductive polymers is very important to toxic gases. If the concentration of the test samples is increased, the conductivity will increase (see Tables IX–XI). When concentration was constant with changing doping time, we saw increased conductivity. In this case, we drew conductiv-

**TABLE IX**  
Conductance Changes for Blend PVAc-PPy

Rel. concentration (ppm)	200	500	800
Cl <sub>2</sub>	0.004	0.0065	0.007
Br <sub>2</sub>	0.006	0.007	0.0085
I <sub>2</sub>	0.0065	0.008	0.0095
HCl	0.005	0.006	0.01
HBr	0.0062	0.009	0.012
HI	0.0085	0.013	0.018
HCN	0.0065	0.007	0.009
MCAA	0.0047	0.006	0.007
TCMB	0.0095	0.015	0.02
BA	0.005	0.0065	0.008
CB	0.0056	0.009	0.0095
MBB	0.0085	0.0095	0.015

$\delta_o = 0.003$  S/cm for different toxic gases and vapors.

**TABLE X**  
Conductance Changes for Blend PS-PPy

Rel. concentration (ppm)	200	500	800
Cl <sub>2</sub>	0.006	0.007	0.0088
Br <sub>2</sub>	0.0087	0.0087	0.0097
I <sub>2</sub>	0.0089	0.0097	0.01
HCl	0.007	0.0072	0.0095
HBr	0.0072	0.0095	0.01
HI	0.0095	0.01	0.012
HCN	0.0085	0.009	0.01
MCAA	0.006	0.006	0.007
TCMB	0.009	0.0095	0.01
BA	0.006	0.0065	0.0065
CB	0.0065	0.007	0.007
MBB	0.007	0.009	0.0095

$\delta_o = 0.005$  stem for different of toxic gases and vapors.

ity of changes of PPy blends to doping time in the constant concentrations (200, 500, and 800 ppm) of gases and vapors tested. These curves are represented in Figures 6–14.

### CONCLUSION

The advantages of this work over our previous works<sup>14–17</sup> are operation at room temperature, decreasing response times, conductance stability for long amounts of time in air, sufficient diffusion of gas into the polymer chain, and better reversibility and processibility. The blends appear to be homogeneous. The blends of PPy have not only higher mechanical strength but also better stability to the action of the environment. The sensoric properties of PPy blends via toxic gases and vapors are better than PPy to hydrogen halides, hydrogen cyanide, and halomethyl compounds,<sup>14</sup> and polyaniline blends are same.<sup>17</sup>

The tested samples are sufficient penetrability into polymer chains, therefore preswelling polymers is lower important. Therefore they are impossible deg-

**TABLE XI**  
Conductance Changes for Blend PVC-PPy

Rel. concentration (ppm)	200	500	800
Cl <sub>2</sub>	0.02	0.025	0.033
Br <sub>2</sub>	0.022	0.028	0.035
I <sub>2</sub>	0.027	0.036	0.045
HCl	0.03	0.04	0.065
HBr	0.035	0.065	0.075
HI	0.045	0.067	0.076
HCN	0.04	0.046	0.067
MCAA	0.022	0.025	0.032
TCMB	0.05	0.075	0.098
BA	0.022	0.029	0.036
CB	0.024	0.033	0.04
MBB	0.045	0.05	0.075

$\delta_o = 0.02$  S/cm for different toxic gases and vapors.

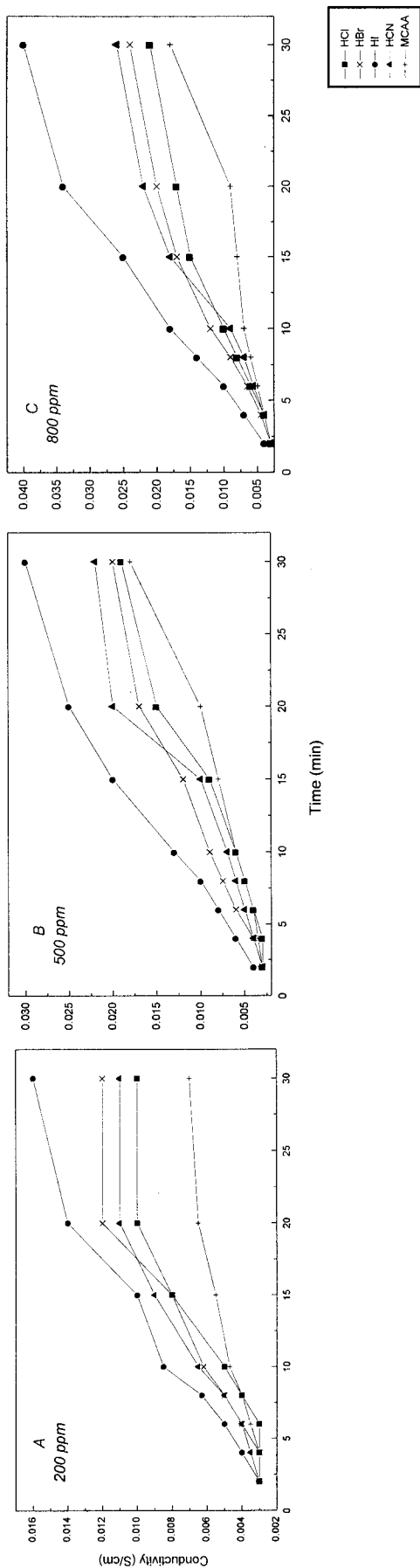


Figure 6 The conductivity of changes of the PVAc-PPy blend;  $\delta_o = 0.003$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of HCl, HBr, HI, HCN, and MCAA at room temperature.

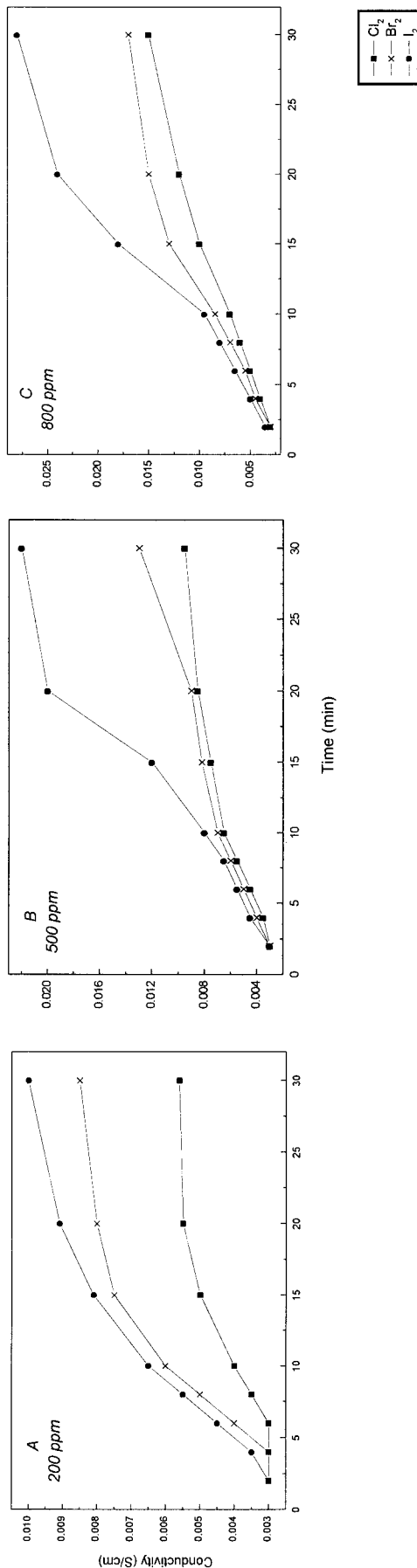


Figure 7 The conductivity of changes of the PVAc-PPy blend;  $\delta_o = 0.003$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> at room temperature.

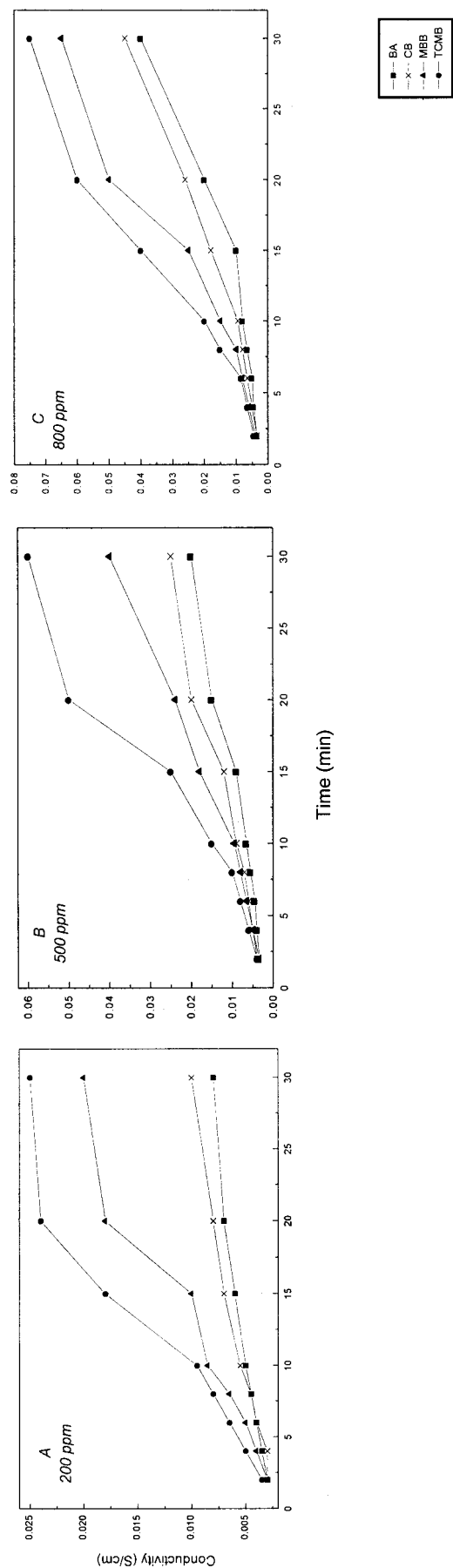


Figure 8 The conductivity of changes of the PVAc-PPy blend,  $\delta_o = 0.003$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of BA, CB, MBB, and TCMB at room temperature.

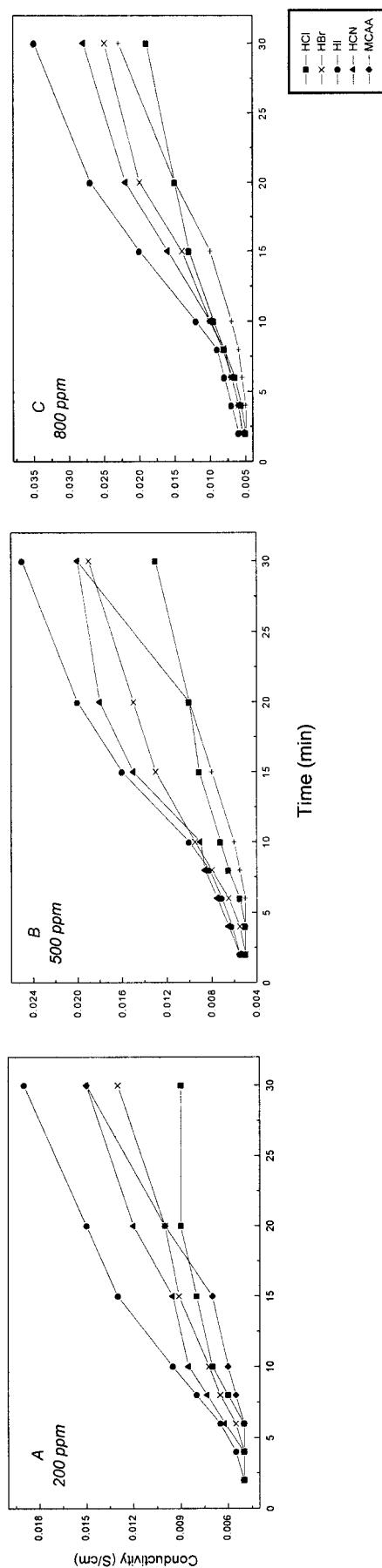


Figure 9 The conductivity of changes of the PS-PPy blend,  $\delta_o = 0.005$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of HCl, HBr, HI, HCN, and MCAA at room temperature.

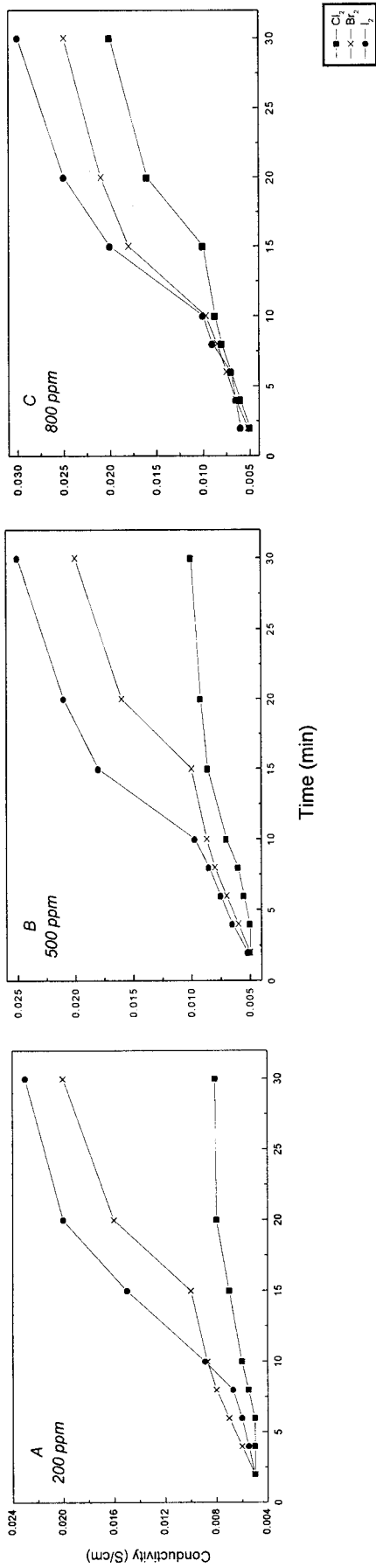


Figure 10 The conductivity of changes of the PS-PPy blend;  $\delta_o = 0.005$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> at room temperature.

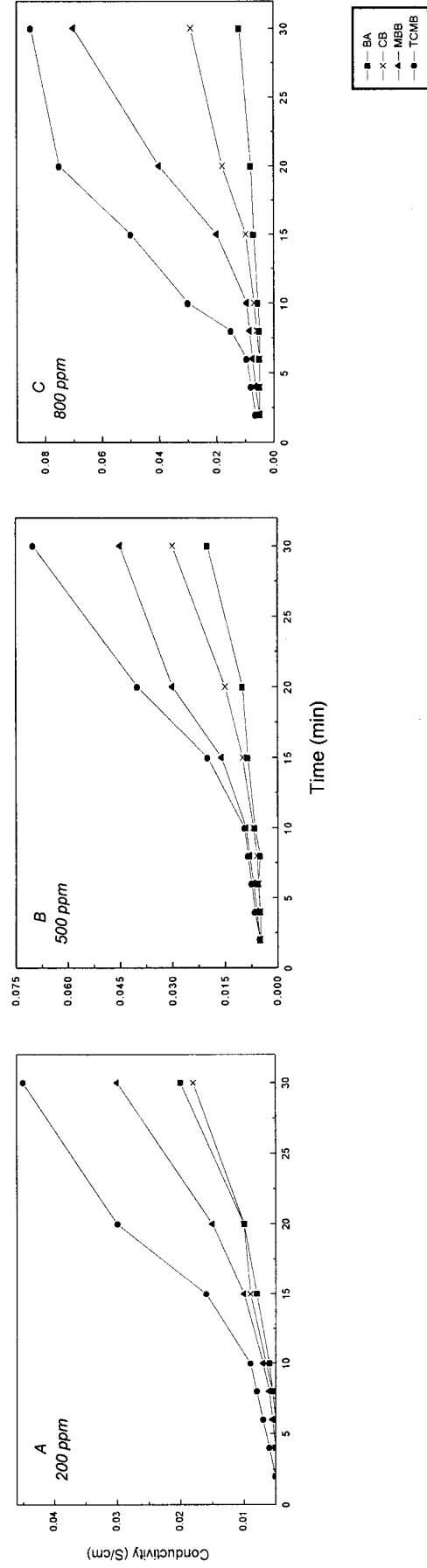


Figure 11 The conductivity of changes of the PS-PPy blend;  $\delta_o = 0.005$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of BA, CB, MBB, and TCMB at room temperature.

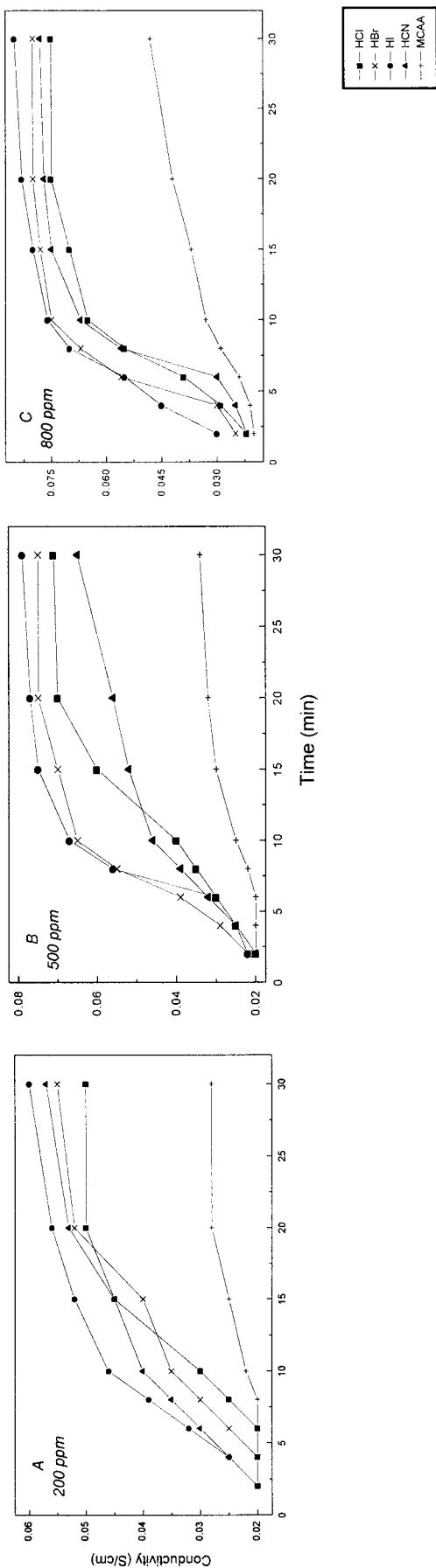


Figure 12 The conductivity of changes of the PVC-PPy blend;  $\delta_0 = 0.02$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of HCl, HBr, HI, HCN, and MCAA at room temperature.

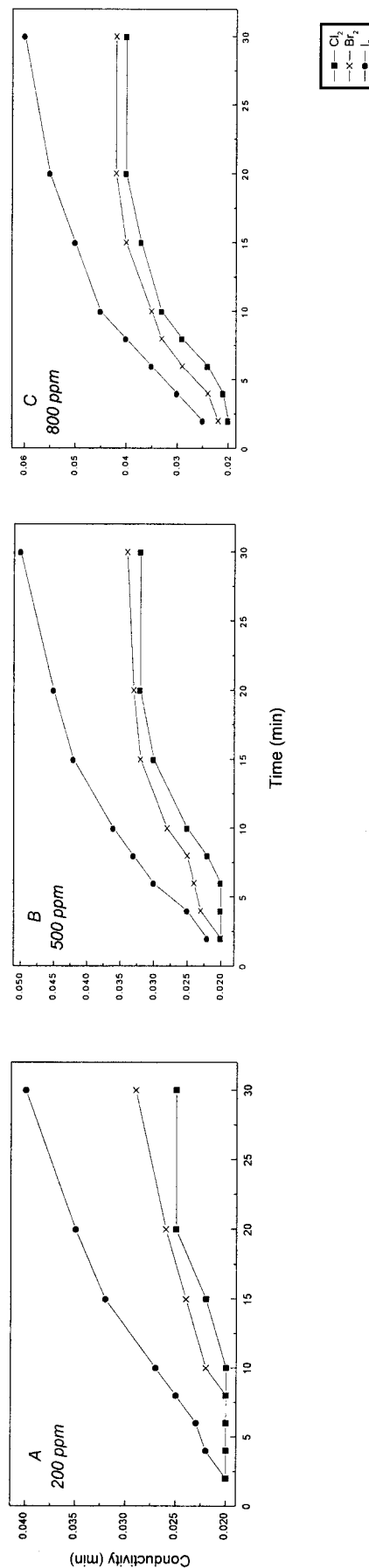


Figure 13 The conductivity of changes of the PVC-PPy blend;  $\delta_0 = 0.02$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> at room temperature.

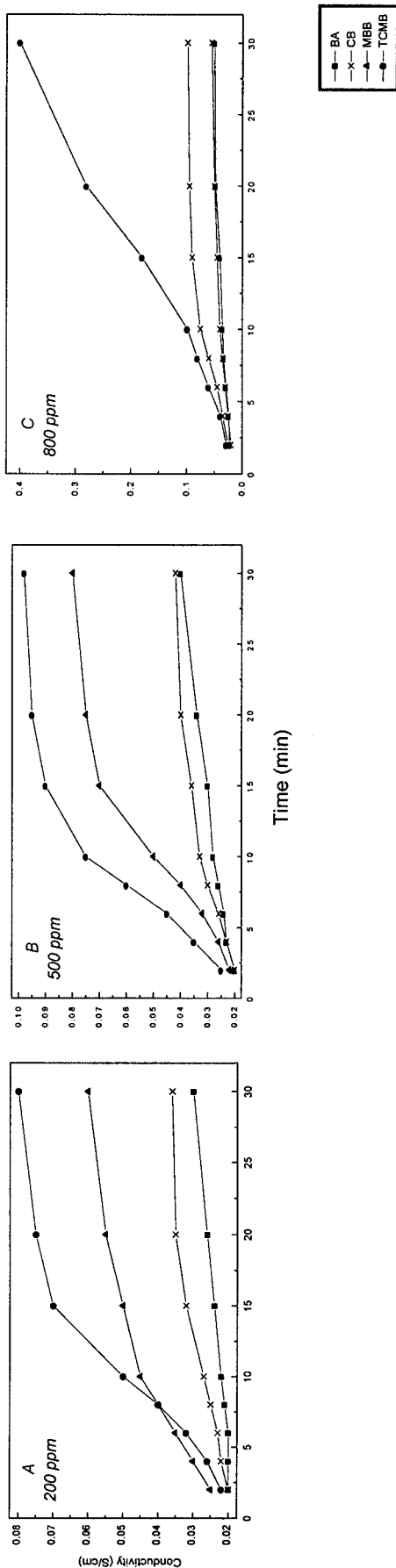


Figure 14 The conductivity of changes of the PVC-PPy blend;  $\delta_o = 0.02$  S/cm versus time for (A) 200, (B) 500, and (C) 800 ppm of BA, CB, MBB, and TCMB at room temperature.

radiation reology and polymer structure and polymer would have recovered. The largest absorption and conductivity are near 800 ppm concentrations. Initial absorption changes and conductivity changes are between 50–100 and 100–200 ppm concentrations, respectively. The PPy blends are good candidates for sensing toxic gases and vapors. These blends are sufficient sensors for hydrogen halides, hydrogen cyanide, and CB, and for MBB and TCMB are the best.

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