Chemical and Electrochemical Synthesis of Conducting Graft Copolymer of Vinyl Acetate with Pyrrole and Studies of Its Gas and Vapor Sensing

S. Hossein Hosseini,[1] Ali A. Entezami[2]

[1]Department of Chemistry, Imam Hossein University, Tehran, Iran
[2]Polymer Lab, Faculty of Chemistry, Tabriz University, Tabriz, Iran

ABSTRACT: Copolymers in general exhibit physical and mechanical properties far different from those of homopolymers and different from those of blends of the same individual homopolymers. Pyrrole (Py) **3** was grafted onto a poly(vinyl acetate) (PVAc) backbone that contained the Py moiety within via chemical and electrochemical oxidative polymerization. Graft copolymer **4** was soluble with low Py amounts but became rapidly insoluble with increasing Py content due to the formation of long Py sequences. The maximum conductivity of films cast from the reaction mixture was 8.3×10^{-3} S/cm. The product **4** was characterized and studied in detail using elemental analysis, ATR, ^{1}H-NMR, UV-visibility, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

Gas sensors based on conducting polymers that exhibit electrical conducting properties can be used as specific toxic gas and vapor detectors. We report here effects of conductance and mass changes onto a graft copolymer **4** after exposure to hydrogen halides, hydrogen cyanide, 1-3-5 trichloromethyl benzene (TCMB), methylbenzyl bromide (MBB), bromobenzyl cyanide (BBC), cyanogen chloride (CC), and cyanogen bromide (CB), using two techniques: a four-point probe method and a X-ray fluorescence (XRF) device, respectively. Increasing of ratio polypyrrole (PPy) in the graft copolymer 4 increase the sensing properties of this copolymer and decrease the solubility of it. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 40–48, 2003

Key words: graft copolymer; conducting polymer; sensors
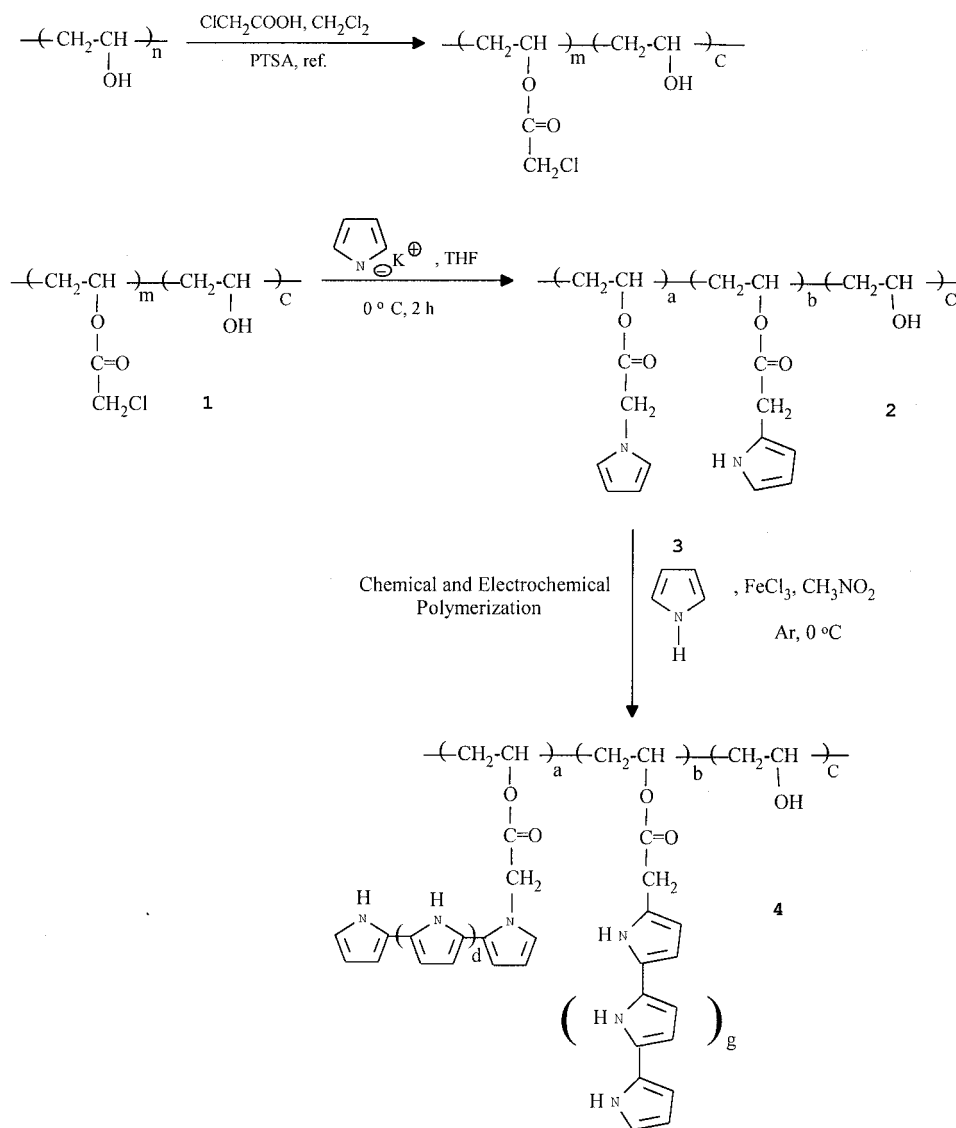
INTRODUCTION

One of the interesting subjects in conducting polymers is the connection of these polymers with base polymers in different properties and creating new properties. These polymers can be connected as block or graft and cause changes in their solubility. The most common approach for this involves electrochemical polymerization of pyrrole (Py) on an electrode that is already coated with insulating polymers.[1–3] The basic aim is to obtain homogeneous composites with good mechanical properties, at least to a certain extent. In these studies low percolation thresholds were achieved with the help of hydrogen bonding between host matrix and polypyrrole (PPy).[4] Graft polymers were also obtained via the chemical polymerization method.[5] The graft polymer films showed different behaviors in differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR) (ATR), as compared with the mechanical mixture of the two polymers. Insolubility of the insulating polymer in a

suitable solvent suggested that the composite may be graft rather than a mixture of two polymers.

Galvin and Wnek[6] reported about conducting solution copolymers from polystyrene block polyethylene. While Baker and his coworkers[7–9] experienced the same result with optics, François and his collaborators[10,11] reported that block and graft copolymers of polystyrene and polythiophene are a good solution with a good amount of conductivity. They also supplied the pure polythiophene with conductivity of 60 S/cm from polymerization of these copolymers. Recently Stanke and his coworkers[12] reported that graft copolymers from poly(methyl methacrylate) and PPy have a good amount of conductivity. These graft copolymers are connected to each other by an ethylene intermediate and they have physical properties and satisfied conductivity.

Copolymers in general exhibit physical and mechanical properties far different from those of blends of the same individual homopolymers. For example, the butadiene-styrene copolymer in a 3:1 ratio (synthetic rubber) has desirable properties that cannot be achieved with either of the homopolymers or any of their blends. The properties of copolymers can also be modified by varying either the ratios of the various constituents or the manner by which they are chemically attached. A large variety of copolymers should thus be obtainable by varying the nature, number, and

Correspondence to: S. Hossein Hosseini (hhoseini@ihu.ac.ir or hosseini65@hotmail.com).

Scheme 1

ratios of the polymers copolymerized with PPy. In this investigation, we point out the production of graft copolymer films of poly(vinyl acetate) (PVAc) and PPy (Scheme 1). Here, we determined the composition as well as the conductivity and solubility properties of graft copolymer **4** depending on the reaction conditions.

The graft copolymer materials prepared from hydrophilic polymers, PVAc, and PPy could be appropriate for various applications in science and technology due to the good mechanical properties and their electrical conductivity. The family of PPy materials can be used for biosensors,[13] chemosensors,[14] electronic devices,[15] and as solid electrolytes in rechargeable batteries.[16] Preliminary investigations to employ these polymers as sensitive materials for gas sensors[17] have been promising and more detailed studies are in progress.

In this article, we will study and analyze the results of this investigation. Because of the vast volume of the investigation we couldn't analyze the quantity of these

polymers as sensors, but the first study and analysis shows that with changes in percentage of Py in the copolymer's structure, the result of sensitivity changes as well. On other hand, changes and maximum balance of doping are limited. However, they have stability of electrical conduction and high physical resistance and acceptable sensitivity in density higher than 200 ppm.

We found that by adding a suitable spacer we can add more percentage of Py in copolymers. In this case we can increase the amount of conductivity by preserving the ratio of physical properties and solubility. Meanwhile, we can decrease its sensitivity down to 200 ppm compared with examined gases.

EXPERIMENTAL

Instruments and materials

Conductivity changes were measured with a four probe device (home made) and mass changes were

measured with X-ray fluorescence (XRF), mode 1, EDXRF 300 link. Elemental analysis was determined with Perkin-Elmer 2400 CHN. A FTIR spectrometer (8101 M-Shimadzu) was used in spectral measurements of the polymer and copolymer films. Cyclic voltammetry and electrochemical polymerization were carried out using a digital potentiostate DP8 (home made). Proton nuclear magnetic resonance (FT-^{1}H-NMR) spectra were recorded at 200 and 400 MHz on a Bruker WP 200 SY spectrometer. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and integration. Visible spectra were obtained by a Perkin-Elmer Lambda 15 spectrophotometer. Molecular weights were measured at 30°C with gel permeation chromatography (GPC) (model 150-C; Walters Associates). Three styragel packed columns with different pore sizes (10^4–10^6 A^0) were used. The mobile phase was tetrahydrofuran (THF) with a flow rate of 1.5 mL/min. The solution concentration was 0.2 wt %. Calibration of the instrument was performed with nine standard samples of monodisperse polystyrene having molecular weights between 3.0×10^3 and 1.4×10^6. The thermal properties of the polymers were studied by thermogravimetric analysis (TGA), DSC of PL Thermal Science. SEM was employed to study the type of surface morphology of polymer. A Cambridge S-360 SEM was used for this purpose.

Py (Aldrich) was dried with NaOH, fractionally distillated under reduced pressure from sodium, or CaH_2. Poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (medium molecular weight; Aldrich) were used as matrix polymer. Acetonitrile (Merck) was dried on silicagel and distilled on P_2O_5 in the presence of nitrogen gas. All the other materials and gases used in this work were purchased from Merck chemicals and purified, or were prepared by methods found in the literature.

Preparation of poly(vinyl chloroacetate) (PVCA)

We equipped a 250 mL three-necked flask with a mechanical stirrer, condenser, and a dropping funnel, and placed a solution of 11 g (0.25 mol) of poly(vinyl alcohol) in 75 mL of di-chloroethane in the flask and 20 mL saturated solution of p-toluene sulfonic acid (PTSA) in di-chloroethane in the dropping funnel.

We added 28.4 g (0.3 mol) mono-chloroacetic acid in 75 mL of di-chloroethane to the flask and produced suspension solution and refluxed for 5 min. Then we added PTSA solution until the solution had a clear appearance. We continued stirring at reflux and room temperature for 3 and 10 h, respectively. The mixture was precipitated in ice ethanol and filtered, and then washing produced solids with acetone and ethanol, which were dried above vacuum (yield = 85%).

UV-visible in THF: λ_{max}; 302 nm (3.9 intensity), 309 nm (3.8 intensity), 359 nm (2.4 intensity), 496 nm (1.39 intensity)

ATR: 3516(m), 2961(sh), 1757(s), 1418(m), 1317(m), 1194(m), 1148(s), 953(m), 785(m), 708(m), 577(sh) cm^{-1}

FT-^{1}H-NMR ($CDCl_3$): δ 4.4(s,sharp,2H), 4.1-(s,sharp,1H), 3.2(s,weak,0.4H), 1.7(s,broad,2H) ppm

Preparation of poly(vinyl pyrroleacetate) (PVPAc)

We dissolved 1.48 g PVAc in 50 mL dry THF, then we equipped a 250 mL three-necked flask with a mechanical stirrer, condenser, and a dropping funnel [containing 2.94 g (0.02 mol) potassium Py[18] in 10 mL dry THF]. The flask was occasionally cooled in an ice-water bath. We added the potassium Py solution dropwise for 30 min while vigorously stirring at 0°C temperature. We continued stirring for a further 2 h and then increased flask temperature to near reflux temperature. We filtered and separated the solution transfer to 100 mL n-heptane and precipitated PVPAc, then filtered it again and dried it above vacuum (total yield 65%).

UV-visible in THF: λ_{max}; 255 nm (3.1 intensity), 305 nm (2.9 intensity), 360 nm (1.8 intensity)

ATR: 3300–3600(br), 3090(sh), 3034(sh), 2940(sh), 2872(sh), 1728(s), 1635(m), 1541(m), 1508(m), 1458(br), 1383(s), 1296(m), 1174(m), 1010(s), 864(w), 800(m) cm^{-1}

FT-^{1}H-NMR ($CDCl_3$): δ 6.95(s,sharp,0.3H), 6.81-(s,weak,0.2H), 6.37(s,sharp,0.6H), 4.82(s,sharp,2H), 4.11(s,sharp,1H), 3.51(s,weak,0.3H), 1.74(s,broad,2H) ppm

Chemical preparation of PVAc-graft-PPy

We prepared a solution of 1 g PVPAc in 30 mL THF in a two-necked, 250 mL round bottomed flask fitted with a dropping funnel under N_2 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. Py was then added in one step to the stirred solution. The molar ratio of $FeCl_3$/Py was chosen to be 3:2 and was kept fixed under N_2 atmosphere during our experiments for 1 h, because it led to a high yield conductivity copolymer.

UV-visible in THF: λ_{max} ; 245 nm (3.8 intensity), 310 nm (3.9 intensity), 530 nm (1.1 intensity)

ATR: 3352(br), 2943(sh), 1736(s), 1589(m), 1412(m), 1312(m), 1192(s), 1049(m), 957(w), 783(m) cm^{-1}

FT-^{1}H-NMR ($CDCl_3$): δ 8.20(s,broad,1.3H), 6.81(s, sharp,0.3H), 6.25(s,sharp,2.4H), 4.75(s,sharp,2H), 4.08(s,sharp,1H), 1.81(s,broad,2H) ppm

Electrochemical preparation of PVAc-graft-PPy

Electrochemical synthesis of PVAc-graft-PPy was carried out using a conventional three electrode system

with a SCE reference, platinum wire counter electrode, and GC disk working electrode.

The solution for electrochemical graft copolymerization was freshly prepared using acetonitrile distilled over P_2O_5 in the presence of inert gas, and it was stored over molecular sieves.

Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was placed under bubbling dry oxygen free nitrogen for at least 20 min before each cyclicvoltammetry. First, we coated a suitable amount of PVPAc on the GC disk electrode using casting method and then we added $10^{-6}M$ Py. Polymer was grown on the GC disk electrode under scan potential in the range of 500–1700 mV and a scan rate of 50 mV/s. The thickness of the film was about 0.7 μm as determined by SEM.

Preparation of PVAc-graft-PPy film

One gram of PVAc-graft-PPy black powder was slowly added (over 30 min) to 20 mL of THF solution and magnetically stirred at room temperature for 5 h. The resulting low viscous solution was prefiltered twice through a Buchner funnel using Whatman paper #541 to remove large particles. Finally it was filtered with Whatman paper #542. The produced low viscous solution of polymer was spread over a piece of glass to obtain an even layer of film, which was then dried under vacuum. In general, slower drying gave film with more uniform thickness. Dried film was removed from the glass by immersion in water. The film prepared from 6 mL of solution cast over a piece of glass (8 $\times$ 8 cm) gave a film with thickness of $\approx$15–25 μm. The conductivity of the polymer measured with the four-probe method was 3.6×10^{-3} S/cm.

Sensor fabrication and toxic gas-vapor generation apparatus

The polymer film prepared in this manner was fabricated for testing the gas sensitivity.[17] For this purpose, the film was fixed onto a glass plate using adhesive tape.

The test gases and vapors were introduced into the sensors with the argon carrier gas in a double impinge exposure cell as described previously.[17,19,20] However, the method of gas and vapor generation was different. A system was designed consisting of a series of needle valves controlling the gas flow rates, which could be monitored via a bank of flow meters. The argon flow constituted the main flow in the cell and was adjustable from 1 to 1000 cm^3 min^{-1}. A test gas and vapor flow, adjustable from 1 to 20 cm^3 min^{-1}, was mixed with the vector argon flow, so by controlling both gas and vapor flows, different dilutions could be made. Target samples were produced in two ways. Organic vapor was generated by bubbling a stream of argon carrier gas (via gas wash bottles) through the volatile liquids [HBr, HI, monochloro acetic acid (MCAA),

1-3-5-trichloromethyl benzene (TCMB), bromobenzyl cyanide (BBC), and methylbenzyl bromide (MBB)], thus producing a continuous flow of saturated vapor, the concentration of which depended on the vapor pressure of the liquid. Analyte samples that are normally in a gaseous state at room temperature were prepared by dilution of 99.8% purity [HCN, HCl, cyanogen bromide (CB), and cyanogen chloride (CC)].

Experimental procedure

Before each experiment, samples were swelled by suitable reagents such as diluted basic and acid solutions or volatile organic solutions, and then heated at 70°C in a 5 mmHg vacuum to desorb the residual solvents and humidity out of the polymer film, which could modify the mass and electrical measurements. This copolymer had good penetrability to gases and vapors, so there was no need for preswelling, the same as in our previous works.[18,20] Then the sample's temperature was regulated at 20°C and a constant gas flow of pure argon was established (100 mL min^{-1}) 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 differentiate dry experiments in samples. Curves of low concentration of samples during conductivity measurements were generated by allowing a stream of Ar gas, into which samples were injected, to pass over 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 techniques, respectively. Target gases and vapor exposure was done with the film still mounted in the probe.

RESULTS AND DISCUSSION

Measurement of PPy percentage in PVAc-graft-PPy

In order to assess the percentage of involved polymers in the produced mixture we used elemental analysis. Assessing the percentage of the mixture is important because in this way we are able to analyze the quantity and quality of condition of electron conductivity in the mixture's properties. In all the mixtures, we could make changes in factors such as density of oxidant, solvent, density of monomers, and changes in polymer, because we intend to get the acceptable condition for use in sensitivity usage. For this reason we studied elemental analysis on reliable films in view of electrical conductivity, stability, and mechanical properties. Since there is no nitrogen atom on the polymer base, PVAc, so by measuring the percentage of nitrogen in elemental analysis we can achieve the percentage of PPy in copolymer. To assess the PPy percentage in copolymer we used the following equation. To begin

with, we will measure percentage of theoretical mass of nitrogen in each monomer unit or base polymer (PVPAc):

Percentage of theoretical mass of nitrogen in polymer

$$= \frac{\text{Molecular mass of nitrogen}}{\text{Mass unit of monomer (vinylpyrrole acetate)}} \times 100$$

Percentage of theoretical mass of

$$\text{nitrogen in polymer} = \frac{14}{149} \times 100 = 9.39$$

Percentage of polypyrrole (%PPy)

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

$$(\% \text{ PPy}) = \frac{1.11}{9.39} \times 100 = 11.8 \tag{1}$$

The produced nitrogen percentage by elemental analysis is 1.11. Therefore, percentage of PPy grafted is 11.8.

Study on results of cyclic voltammetry

Figures 1 and 2 illustrate cyclic voltammograms of graft electro polymerization of Py to PVAc and it's blank in the above condition, respectively. As is shown in Figure 1, oxidation potential of Py in copolymer is lower than its potential in homopolymer, PPy, that has been appeared in area above 1500 mV in the 50 mV/s scan rate.

In the next curves, gradually the intensity of the oxidation peak has decreased and grows in direct
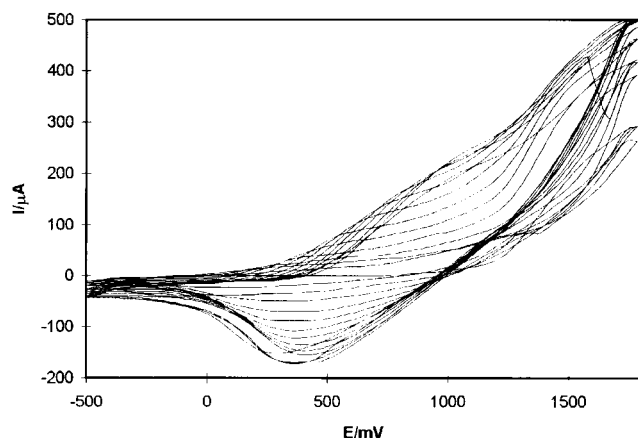
Figure 1 Cyclic voltammograms of formation of vinyl acetate-pyrrole graft copolymer on supporting polymer (poly vinyl chloroacetate) (15 cycles).
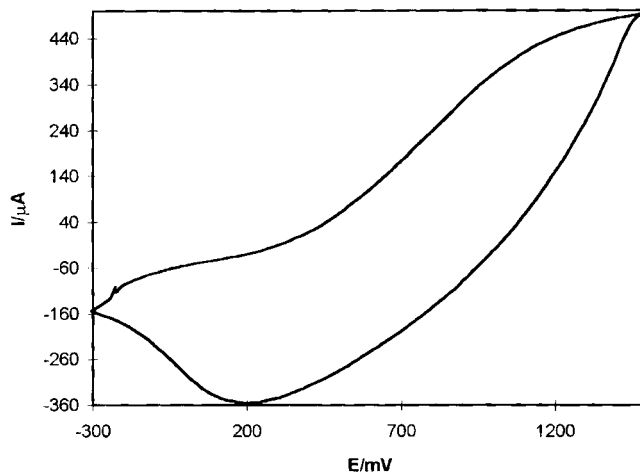
Figure 2 Cyclic voltammogram *of* vinyl acetate-pyrrole graft copolymer (with 18 wt. % PPy, $\delta_0 = 1.9 \times 10^{-3}$ S/cm) in CH_3CN, 0.1 M Bu_4NPF_6, GC disk electrode versus SCE, scan rate = 50 mV/s.

proportion to those reductions and oxidations of grafted polymer peaks, which appear in areas 400 and 1000 mV. Figure 2 illustrates a cyclic voltammogram of graft copolymer of PVAc-graft-PPy. The oxidation-reduction potentials of the copolymer are different from its homopolymer. Therefore, cyclic voltammograms confirm that formation of copolymer. Spectroscopy data also certify the formation of copolymer at the chemical polymerization. As it shows in the voltammogram, PVAc-graft-PPy has suitable reversibility and stability on the electrode's surface. Figure 3 shows the anodic (ipa) and cathodic (ipc) peak currents via different scan rates (Ag/AgCl reference electrode) of PVAc-graft-PPy. The curves are linear; therefore, the polymers are stable on the electrode surface and redox of reaction polymer film on the electrode surface has surface absorption.

Study on results of DSC and TGA

Figure 4 illustrates the thermograms of STA (DSC and TGA) PVAc-graft-PPy. Comparison of these thermograms with STA thermograms of PVAc specifies that softening, melting points and heating resistance of the produced copolymer are higher than when they haven't been grafted.

As it shows in PVAc-graft-PPy thermogram, when it was less than 100°C this polymer started to soften and up to 158.3°C it lost approximately 4.5% of its weight, which was due to humidity and existing solvent or part of HCl in the chain polymer, and at 337.5°C it lost approximately 35% of its total weight. This temperature is a primary distraction temperature of polymer and it is the stability temperature of polymer, and at 475.3°C the polymer starts its complete distraction, which continues to 600°C.
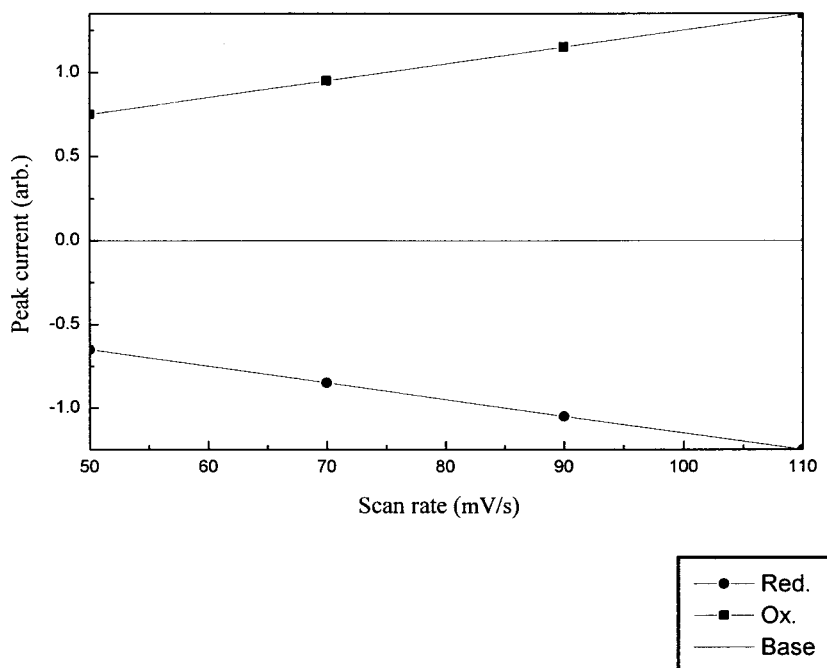
Figure 3 The anodic and cathodic peak current versus scan rate of PVAc-graft-PPy.

Study on results of SEM and GPC

Figure 5 shows the image of SEM of PVAc-graft-PPy. As it shows in this figure, monotony and single phase of polymers completely clear and Py's granulate particles in polymer's surface have been grown well and monotony. PPy shows a spongelike morphology in contrast to PVAc-graft-PPy, which has smooth surfaces, and no morphological characteristics of PPy could be observed in it. Earlier studies on the surface

morphology of PVAc have demonstrated its smooth surface. Despite the fact that PVAc-graft-PPy contained about 11.8 wt % PPy, according to elemental analysis determination, no free PPy was seen in the SEM picture of the graft copolymer. This observation enforces the assumption that covalent bonds between PVAc and PPy chains were produced.

The GPC of PVAc-graft-PPy was analyzed using polystyrene standard. The GPC curves obtained show
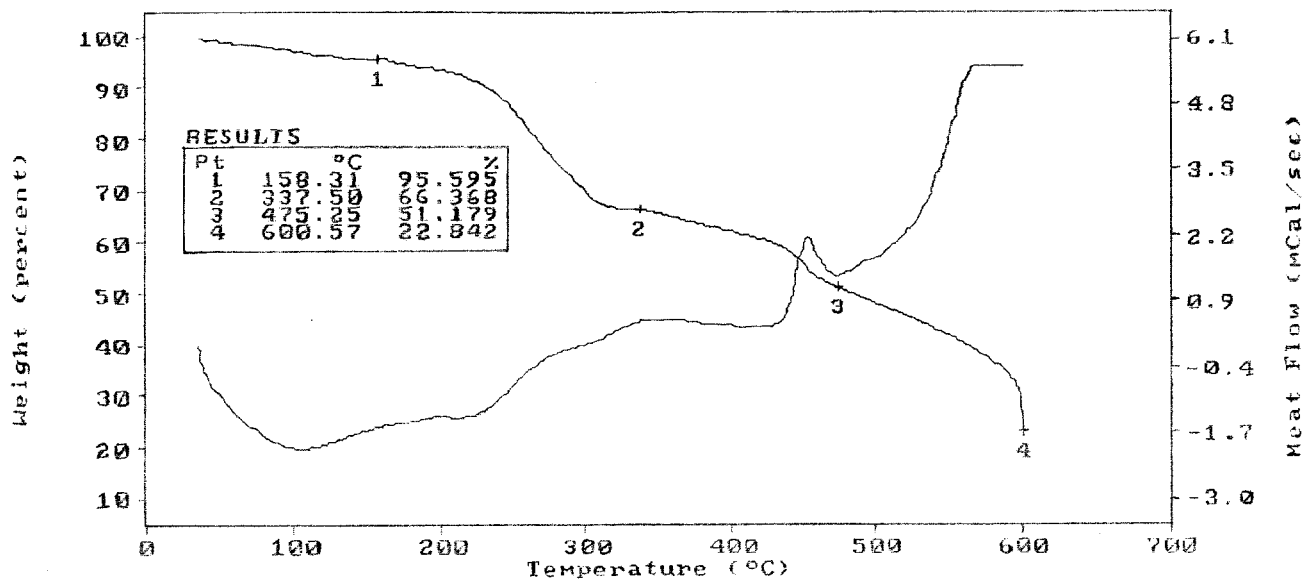

Figure 4 STA (DSC and TGA) thermograms of PVAc-graft-PPy.
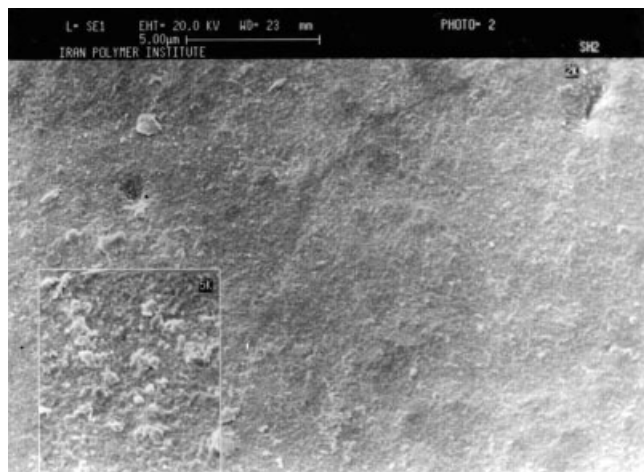
Figure 5   SEM micrograph of PVAC-graft-PPy.

a unimodal distribution. The molecular weight distribution averages for the polymer are presented in Table I.

Conductivity and mass measurements

The results of XRF measurements of PVAc-graft-PPy film are reported in Table II. Chlorine arises from a dopant anion and Cl_2, and Br_2 existence is related to the presence of gases containing halogen in the polymer chain. When the concentration of test samples increases, the concentrations of Cl_2 and Br_2 increase. Table III shows the conductance measurements of PVAc-graft-PPy, which are affected by different concentrations of toxic gases and vapors. The resistivity of PVAc-graft-PPy decreases upon exposure to tested samples. The conductivity changes upon exposure to these relatively small gas and vapor concentrations are almost reversible. When higher concentrations of samples are used, the conductivity changes become smaller and partly irreversible. The results in the tables show that the tested samples were exposed to the produced gases and vapors after 10–20 min.

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 Table III). If the concentration is left constant with changing doping time, the conductivity

TABLE I
Molecular Weight Distribution Averages
for the PVAc-graft-PPy

Molecular weight data	PVAc-graft-PPy
Number average	26709
Weight	77757
Z average	173163
Z+1 average	282263
Polydispersity	2.9
Molecular wt.	57278

TABLE II
Mass Changes Determined by XRF Method
for PVAc-graft-PPy

Relative concentration (ppm)	200	400	600
HCl	0.47	0.91	1.5
HBr	1.3	2.1	3.1
HI	2.2	4.1	7.5
CC	0.41	0.71	1.2
CB	0.45	0.82	1.7
TCMB	0.52	1.3	3.1
MBB	0.33	0.52	1.3
BCC	0.38	0.82	1.8

[a] Mass changes are measured by relative percentage Halogen.
[b] PVAc-graft-PPy for concentration of samples; X-ray; 0–20 KeV; intensity; 2000–6000 cts.

is increased. In this case, we are drawing conductivity of changes of PVAc-graft-PPy to doping time in the constant concentrations (200, 500, and 800 ppm) of gases and vapors tested. These curves are represented in Figures 6–8.

CONCLUSION

PVAc-graft-PPy is a conductive and soluble polymer that has new physical properties such as its desirable solubility and conductivity, it will have proper sensitivity effects. Although these polymers have low electric conductivity, they easily react and show sensitive effects against gases. In order to decrease the reflected time we did not need to preswell the polymers.[18,20] These polymers will be able to be swelled by primary concentrations of gas and by increasing the speed of diffusion of gas inside the polymer. Results of studying these polymers indicate that they have good stable conductivity and nearly high resistance against factors such as air atmosphere, humidity, and so forth, but primary changes in their conduction are low. Experience shows that by adding ethylenic spacer between grafted branch and base polymer, we can add more Py's to the backbone copolymer, and by increasing

TABLE III
Conductance Changes for PVAc-graft-PPy

Relative concentration (ppm)	200	400	600
HCl	0.0042	0.0054	0.0070
HBr	0.0047	0.0072	0.015
HI	0.013	0.02	0.029
HCN	0.005	0.007	0.008
CC	0.0041	0.0054	0.0068
CB	0.005	0.0061	0.0075
TCMB	0.008	0.019	0.025
MBB	0.0052	0.0062	0.0082
BCC	0.0089	0.022	0.03

[a] $\delta_0 = 3.6 \times 10^{-3}$ S/cm for different of toxic gases and vapors.
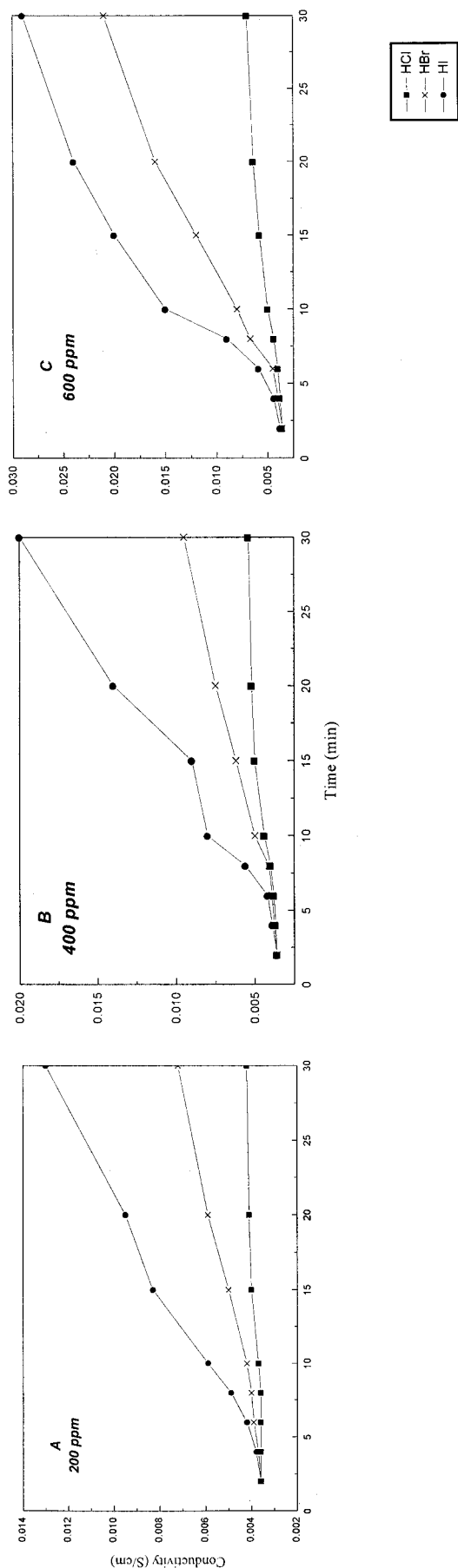
Figure 6 The conductivity changes of PVAc-graft-PPy; $\delta_0 = 0.0036$ S/cm versus time for (A) 200, (B) 400, and (C) 600 ppm of HCl, HBr, and HI at room temperature.
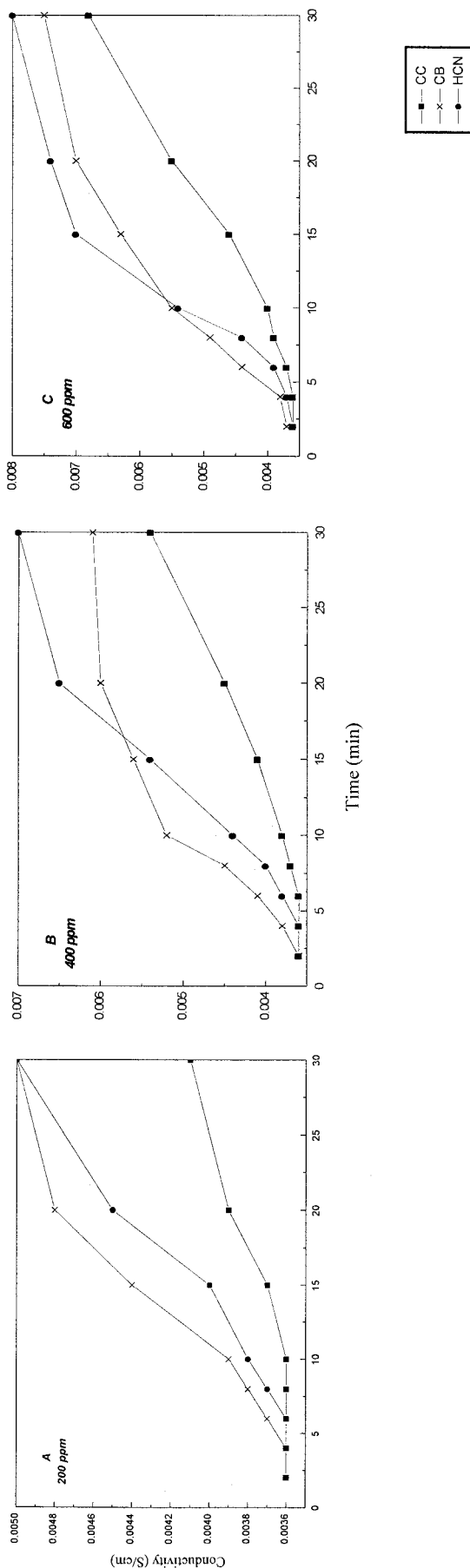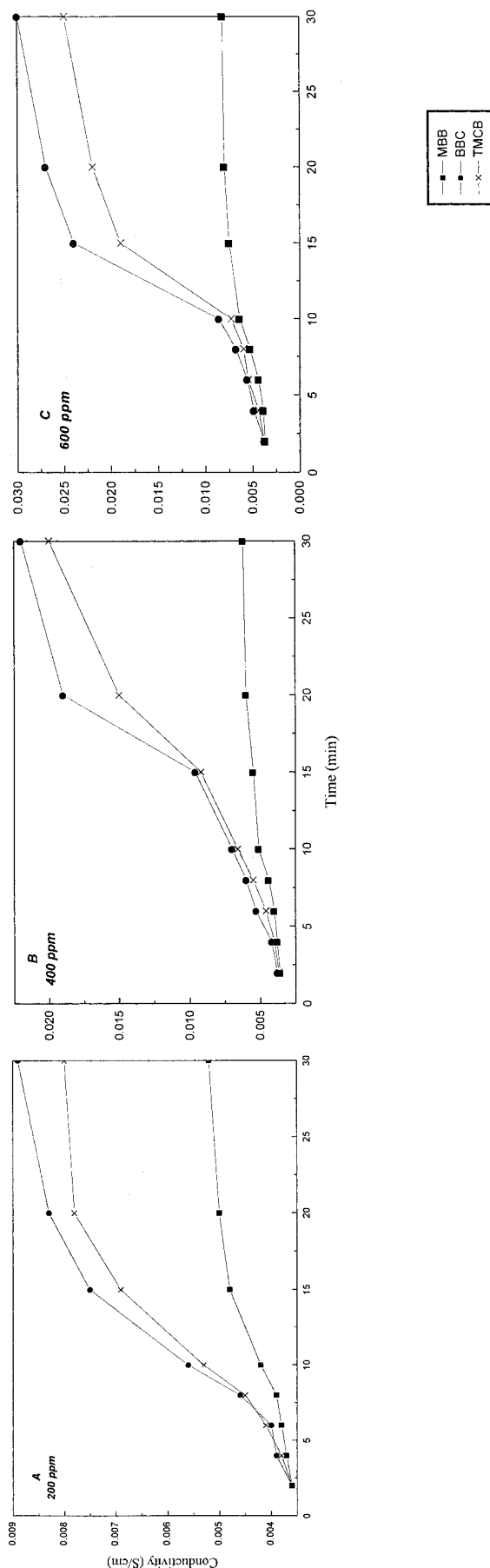
Figure 7 The conductivity changes of PVAc-graft-PPy; $\delta_0 = 0.0036$ S/cm versus time for (A) 200, (B) 400, and (C) 600 ppm of CC, CB, and HCN at room temperature.

Figure 8 The conductivity changes of PVAc-graft-PPy; $\delta_0 = 0.0036$ S/cm versus time for (A) 200, (B) 400, and (C) 600 ppm of MBB, TMCB, and BBC at room temperature.

polymer conduction and the doping situation the polymer's sensitivity properties can be increased.

References

1. Tieke, B.; Gabriel, W. Polymer 1990, 31, 20.
2. Zinger, B.; Kijel, D. Synth Met 1991, 41–43, 1013.
3. Zhang, G. P.; Bi, X. Synth Met 1991, 41, 251.
4. Wang, H. L.; Toppare, L.; Fernandez, J. E. Macromolecules 1990, 23, 1053.
5. Selampinar, F.; Akbulut, U.; Yalcin, T.; Suzer, S.; Toppare, L. Synth Met 1994, 62, 201.
6. Galvin, M. E.; Wnek, G. E. Polym Commun 1982, 23, 795.
7. Bates, F. S.; Baker, G. L. Macromolecules 1983, 16, 704.
8. Baker, G. L.; Bates, F. S. Macromolecules 1984, 17, 2619.
9. Van Nice, F. L.; Bates, F. S.; Baker, G. L.; Caroll, P. J.; Patterson, G. D. Macromolecules, 1984, 17, 2626.
10. Olinga, T.; Francois, B. Macromol Chem Rapid Commun 1991, 12, 575.
11. Francois, B.; Olinga, T. Synth Met 1993, 55–57, 3489.
12. Stanke, D.; Hallensleben, M. L.; Toppare, L. Synth Met 1993, 55–57, 1108.
13. Geckeler, K. E.; Muler, B. Naturwissenchaften 1993, 80, 18.
14. Zhou, R.; Geckeler, K. E.; Gopel, W. In Chemical Sensors in Polymeric Materials Encyclopedia; Salamone, J. C., Ed.; CRC Press: Boca Raton, 1996; 2, 1164.
15. Gazard, M. In Handbook of Conducting Polymers; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; 1, 673.
16. Bittihn, R.; Ely, G.; Woeffler, F.; Munstedt, H.; Naarmann, H.; Naegele, D. Makromol Chem Macromol Symp 1987, 8, 51.
17. Hosseini, S. H.; Entezami, A. A. Iranian Polym J 1999, 8, 205.
18. Hosseini, S. H.; Entezami, A. A. Eur Polym J 1995, 31, 635.
19. Hosseini, S. H.; Entezami, A. A. Polym Adv Technol 2001, 12, 482.
20. Hosseini, S. H.; Entezami, A. A. Polym Adv Technol 2001, 12, 524.