Investigation of Sensing Effects of Polystyrene-graft-Polyaniline for Cyanide Compounds

S. Hossein Hosseini

Department of Chemistry, Imam Hossein University, Babaee Expressway, Tehran, Iran

Received 2 July 2005; accepted 16 June 2005
DOI 10.1002/app.22874

ABSTRACT: Polyaniline and its derivatives have high antioxidative stability and are considered to belong to the most useful conductive polymers for practical application. In this work, we have linked 1,4-phenylenediamine to poly(styrene-*co*-chloromethylstyrene) and prepared poly(styrene-*co*-*p*-aminoanilinemethylstyrene), poly(S-*co*-PAAMS). Polystyrene-*graft*-polyaniline, (PS-*g*-PANi), has been synthesized by adding solution of ammonium persulfate and *p*-toluenesufonic acid in water. The conductivity of these polymers was measured by the four-point probe method. The copolymers produced exhibit electrical conductivity comparable to that of polyaniline. PS-*g*-PANi was also exposed to some cyanide compounds such as hydrocyanic acid (Hydrogen cyanide-HC), ethanedinitrile (Cyanogen-CY), cyanogen chloride (Chlorocyan-CC), and cyanogen bromide (Bromocyan-BC). The cyanide compounds are classified as blood agents groups, in terms of chemical warfare agents standards. First, we prepared different concentration of blood agents at 50, 100, and 150 ppm and exposed them on PS-*g*-PANi for 2 min. Second, we have drawing conductivity change curves *versus* time and produced optimum conductivity versus time taken. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3920–3926, 2006

Key words: graft copolymer; polyaniline; gas sensor; polystyrene; cyanides

INTRODUCTION

The conducting polymers are good candidates for developing chemical or electrochemical sensors in two main ways. (1) As sensitive components, the electronic conductivity, related to the redox state (doping level) of a conducting polymer, is modulated by the interaction with various substrates. Changes in parameter values, such as resistance, current, or electrochemical potential, give a straightforward sensor response of the studied phenomena. (2) As a matrix for specific immobilization, the conducting polymers are often infusible and insoluble. Consequently, immobilization by entrapment of specific molecules that are capable of substrate recognition can be carried out mainly during polymerization process. However, this growing reaction added to the entry of negatively charged species (sometimes positive ones) and makes it possible to entrap various moieties easily in a one step process, with the further advantages of intrinsic porosity and electronic accessibility. In its simplest form, a sensor consists of a planar interdigital electrode coated with a conducting polymer thin film. If a particular vapor is absorbed by the film and affects the conductivity, its presence may be detected as a conductivity change.[1–4] The first evaluation of conducting polymer as sensitive components in chemical sensors are based on their redox interaction with some gases, including a variation of the doping level, resulting in a quite straight forward conductance, monitoring of gas sensor response over orders of magnitude.[5] Interdigited electrodes covered by a polypyrrole (PPy) layer have been tested by Miasik et al.[6] for the detection of NH3, NO2, and H2S gases. Yoneyama et al.[7] have shown that the electropolymerized PPy films exhibit noticeable gas sensitivities to electron acceptor gases such as PCl3, SO2, and NO2 at room temperature, especially when PPy is reduced electrochemically before exposure. The same group also investigated the gas sensing properties of polythiophene film,[8] but they found a more irreversible behavior in the conductivity change after exposure to NH_3 and H_2S.

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, which 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 ratios of the polymers copolymerized with PPy.

In this investigation, we explored the production of graft copolymer films of polystyrene and polyaniline.

Correspondence to: S. H. Hosseini (hhoseini@ihu.ac.ir).

Journal of Applied Polymer Science, Vol. 101, 3920–3926 (2006)

We determined the composition, as well as the conductivity and solubility properties, of those graft copolymers PS-*g*-PANi, depending on the reaction conditions.

The graft copolymer materials prepared from hydrophilic polymers, PS-*g*-PANi, could be appropriate for various applications in science and technology because of the good mechanical properties and their electrical conductivity. The changes and maximum balance of doping are limited, but they have stability of electrical conduction and high physical resistance and acceptable sensitivity in density higher than 100 ppm. We found that, by adding a suitable spacer, one can add more aniline in copolymers.[9] In this case, we can increase the amount of conductivity by preserving the ratio of physical properties and solubility. Meanwhile, we can increase it's sensitivity down to 100 ppm compared with examined gases. Cyanide agents are very dangerous compounds that are called "blood agents" and used as chemical warfare agents. So, we would like detect these compounds in low concentrations for human safety.

EXPERIMENTAL

Instruments and materials

Elemental analysis was determined with Perkin–Elmer 2400 CHN. A Fourier-transform infrared spectrometer (8101M-Shimadzu) was used in spectral measurements of the polymer and copolymer films (sh, sharp; w, weak; m, medium; s, short; b, broad). Conductivity changes were measured with four-probe device (ASTM Standards, F 43–93). Nuclear magnetic resonance (FT-^{1}H and ^{13}C NMR) spectra were recorded at 250 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. UV–visible spectra were obtained by Perkin-Elmer Lambda 15 spectrophotometer. Molecular weights were measured at 50°C with a gel permeation chromatograph (GPC) (Maxima 820 GPC Analysis Report). Three styragel packed columns with different pore sizes (10^4–10^6Å) were used. The mobile phase was *N*,*N*-dimethylformamide (DMF) with flow rate of 1.5 mL min^{-1}. 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 polymer were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, PL Thermal Science). Scanning electron microscopy (SEM) was employed to study the type of surface morphology of polymer. A Cambridge S-360 SEM was used for this purpose.

Aniline (GPR) was dried with NaOH and fractionally distilled under reduced pressure from sodium or CaH_2. Polystyrene with 5 wt % polybutadiene (Aldrich, medium molecular weight) was used as matrix polymer. Dimethylsulfoxide (DMSO, Merck) was dried on molecular sieves (3 Å, 1/16-inch pellets) and distilled on P_2O_5 in the presence of nitrogen gas. 1,4-Phenylenediamine (Aldrich) was purified by recrystalization in ethanol. All the other materials and gases used in this work were purchased from Merck chemicals and purified, or were prepared by literature methods.

Preparation of 1,4-bis(chloromethoxy)butane

Paraformaldehyde (4 g) and 6 g of 1,4-butandiol were mixed together in a flask. The mixture was cooled to about 7°C in a cold water bath, and hydrogen chloride gas was passed into the flask for 7 h. The mixture was then chilled to 0°C overnight, during which time it separated into two layers. The upper layer was collected, washed, dried with magnesium sulfate, and vacuum distilled to yield 58 g of 1,4-bis(chloromethoxy)butane.[10]

Preparation of poly(styrene-*co*-*p*-chloromethylstyrene), poly(S-*co*-PCMS)

To a stirred suspension of 1 g (0.01 mol) of polystyrene and 3.74 g (0.02 mol) of the 1,4-bis(chloromethoxy)butane in 20 mL of methylene chloride was slowly added 0.5 mL (0.0044 mol) of stannic chloride at 0°C. The reaction mixture was stirred at room temperature overnight (16–18 h). The mixture was then cooled to 0°C and treated with 30 mL of 1*N* hydrochloric acid. The polymer beads were recovered by filtration, washed with water-dioxane, dioxane, methanol, and methylene chloride. The beads were dried overnight in vacuum at room temperature. The resulting beads were analyzed for chlorine content.

UV (DMSO) $\lambda_{max} = 225$ nm (4.2 intensity), 275 nm (1.9 intensity). FTIR 3010(m), 2990(m), 1605(m), 1598(sh), 1482(sh), 1440(m),1359(b), 1063(w), 1021(w), 748(s),691(m), and 533(s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.5–7.5 (b and d, 8H), 3.43 (s, 2H), 1.88 (b and m, 1H), 1.46 (b, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ 145, 128, 127, 125, 67.4, 40.4, 29.3 ppm. Elemental analysis: 20.2% (2.83 mmol of Cl/g)

Preparation of poly(styrene-*co*-*p*-aminoanilinemethylstyrene), poly(S-*co*-PAAMS)

A 250 mL three-necked flask containing 30 mL DMF/dichloromethane (50/50 v/v) and 1.5 g poly(S-*co*-PCMS) was equipped with a mechanical stirrer and maintained at temperature of 75°C by an external water bath. Then, 1 g (0.01 mol) 1,4-phenylenediamine, 2 g anhydrous pulverized sodium carbonate, and 5 mL pyridine were added to the flask and the resulting mixture was stirred and heated for 3 h. At the end of this time, the polymer solution was filtered and precipitated into ice methanol, and the product was washed with methanol and dried under vacuum.

UV (DMSO) λ_{max} = 225 nm (4.5 intensity), 278 nm (2.2 intensity), 315 nm (0.7 intensity). FTIR 3450(b), 3015(sh), 3005(w), 2950(sh), 1607(sh), 1550(w), 1485(sh), 1441(sh), 1365(m),1070(m), 1020(m), 755(m), and 690(s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.5–7.5 (b and d, 12H), 4.8(b, 2–3H) 3.38 (b, 2H), 1.86 (b, 1H), 1.43 (b, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ 145, 128, 127, 125, 96.4, 94.5, 67.1, 40.1, 29.2 ppm.

Preparation of polystyrene-*graft*-polyaniline (PS-*g*-PANi)

Poly(S-*co*-PAAMS) (0.5 g) was completely dissolved in 30 mL of DMSO. One gram aniline and 0.5 g *p*-toluensulphonic acid were added to the solution, and then the mixture was vigorously stirred and temperature reduced to 5°C. In a separate container, 2 g (8.77 mmol) $(NH_4)_2S_2O_8$ (ammonium peroxydisulphate) was dissolved in 10 mL tosic acid solution. The oxidant solution was slowly added at a rate of ~5 mL/min to the mixture.

After the mixture was allowed to stir for 10 min, a solution containing 1 g sodium sulfite in water/DMSO was added to the mixture. The mixture was stirred for about 2 h, the polymer solution filtered using G2 sintered glass filter, and then precipitated into ice methanol. The product was washed successively by distilled water and methanol and dried at 60°C for 24 h (Scheme 1).

UV (DMSO) λ_{max} = 220 (2.8 intensity), 280 nm (3.5 intensity), 320 nm (2.8 intensity), 620 nm (1.2 intensity). FTIR 3502(b), 3010(s), 2980(m), 1610(m), 1555(w), 1500(m), 1480(sh), 1460(sh), 1440(sh) 1360(m), 1070(sh), 1015(m), 755(s), and 680(m) cm^{-1}. ^1H NMR (d_6-DMSO) δ 6.5–7.5 (b and m-d, 17H), 4.6−4.8 (b, 8H), 3.72 (s, 2H), 1.84 (b, 1H), 1.54 (b, 2H) ppm. ^{13}C NMR (d_6-DMSO) δ 145.2, 143.0, 140.0, 139.0, 135.6, 121.4, 120.7, 116.6, 115.6, 68.1, 40.5, 30.1, 29.6, 28.9 ppm.

Sensor fabrication and toxic gas–vapor generation apparatus

The polymer film prepared in this manner was fabricated for testing the gas sensor.[11] For this purpose, film was prepared by using adhesive tape and fixed onto a glass plate. The test gases and vapors were introduced into the sensors with the argon carrier gas in a double impingement exposure cell as described previously.[9,11,12] 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}, were mixed with the vector argon flow, so that by controlling both gas and vapor flows, different dilutions could be made. Target samples were produced in two ways. Cyanide compounds were generated by bubbling a stream of argon carrier gas (*via* gas wash bottles) through it, thus producing a continous flow of saturated vapor, the concentration of which depended on the vapor pressure of the liquid. Analyte samples, which are normally in a gaseous state at room temperature, were prepared by dilution of 99.8% purity.

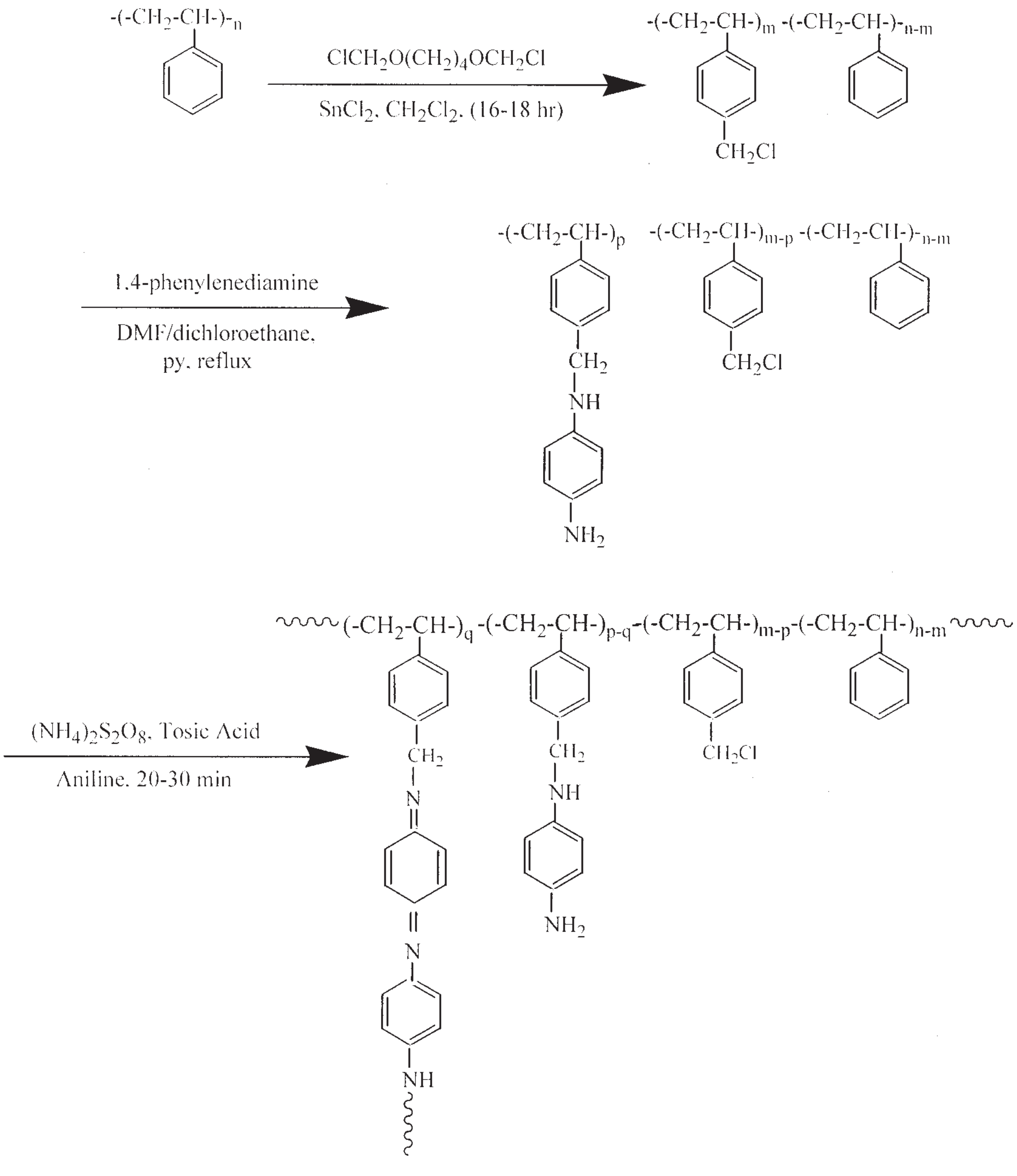
Experimental procedure

This copolymer had good penetrability to gases and vapors, so there was no need for preswelling, the same as our previous work.[12–14] 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 an Ar atmosphere (200−2000 ppm) when they were transferred from the preparation to the measurement equipment. Vapors and gases were sufficiently dry (moisture ≤ 0.6 ppm) to differentiate dry experiments on samples. Curves of low concentration of samples during conductivity measurements were generated by allowing a stream of Ar gas, into which samples was injected, to pass over film. The amounts of gases and vapors were regulated by a magnetic valve and a high-percision flow regulator. Conductivity was measured using four-probe technique. Target gases and vapors exposure were done with the film still mounted in the probe.

RESULTS AND DISCUSSION

Measurement of PANi percentage in PS-*g*-PANi

To assess the percentage of involved polymers in produced mixture, we use elemental analysis. Assessing the percentage of the mixture is so important because in this way, we are able to analyze the quantity and quality of condition of electron conductivity in mixture's properties. In all the mixtures, we made changes in factors, such as density of oxidant, solvent, density of monomers, and changes in polymer to get the acceptable conditions for sensitivity usage. For this reason, we studied elemental analysis on reliable films in view of electrical conductivity, stability, and mechanical properties. If each styrene ring had received one chloromethyl group, the resulting product would have had a chloride content of 23.2%. Elemental analysis for poly(S-*co*-PCMS) showed 20.2% (2.83 mmol of Cl/g), which means that 86% of the rings were chlo-



Scheme 1

romethylated. Since PS is without a nitrogen atom, by measuring the percentage of nitrogen by elemental analysis, we can determine the percentage of PANi in the copolymer. To assess the aniline and PANi percentages in copolymer, we use the following equations. In the beginning, we will measure percentage of theoretical mass of nitrogen in each monomer unit or base polymer poly (S-co-PAAMS) and then on PS-g-PANi.

$$\text{Percentage of theoretical mass of nitrogen in polymer} = \frac{\text{Molecular mass of nitrogen}}{\text{Mass unit of monomer (p-aminoanilinemethylstyrene)}}100$$

$$\text{Percentage of theoretical mass of nitrogen in poly}(S\text{-}co\text{-PAAMS}) = \frac{14}{224}100 = 6.25$$

$$\text{Percentage of aniline in copolymer poly }(S\text{-}co\text{-PAAMS})\ (\%\text{aniline}) = \frac{\%\text{N Found}}{\text{Theoretical mass of nitrogen in polymer}}100$$

$$(\%\ \text{aniline}) = \frac{12}{6.25}100 = 192$$

$$\frac{192}{2} = 96$$

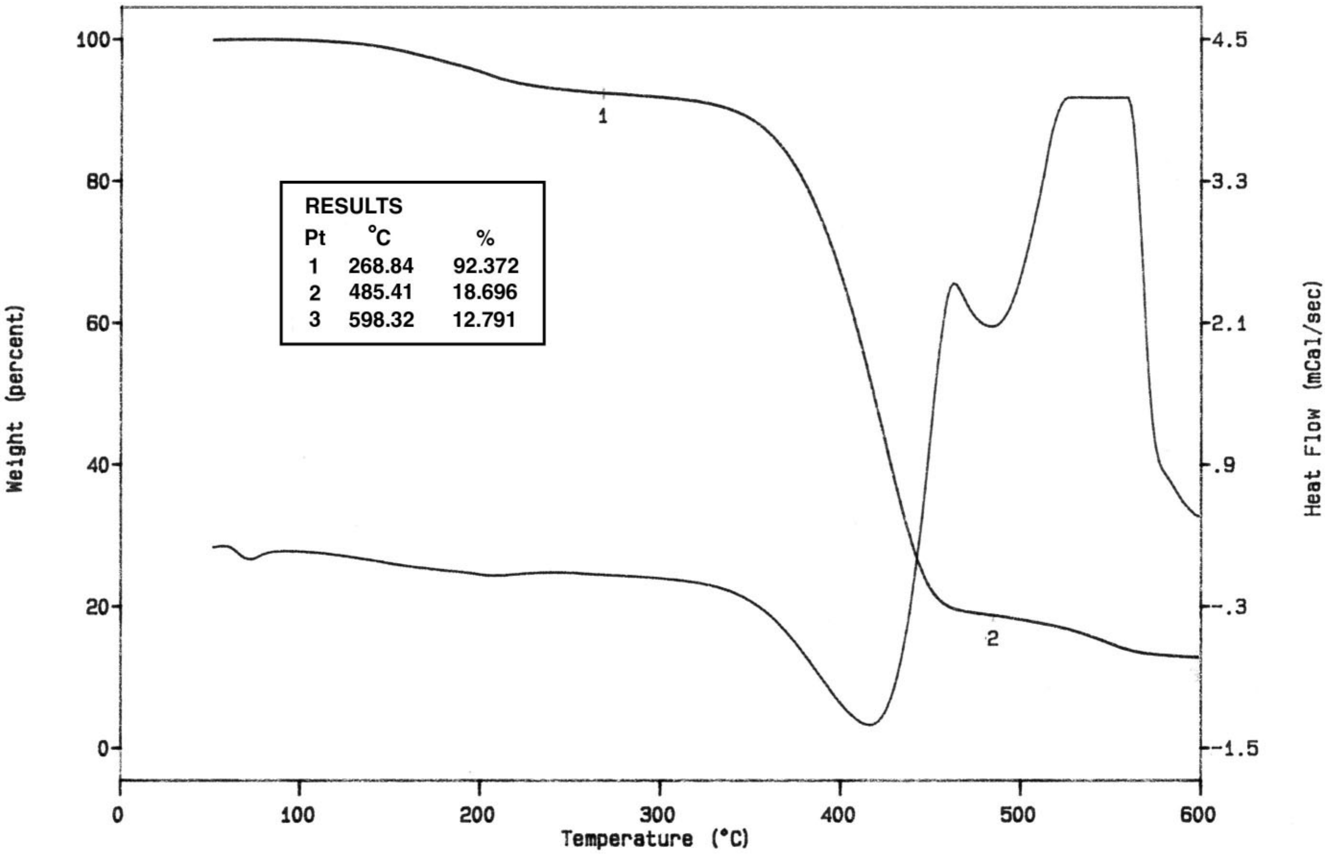


Figure 1 STA (TGA and DSC) thermograms of PS-*g*-PANi

which means that 96% of the chloromethylated rings were phenylaminated. On the other hand, for calculation of percentage of PANi on graft copolymer, we measured according to the following equations. We know that percentage of nitrogen after grafting is 22.5, so

$$\text{Percentage of aniline or PANi in PS-}g\text{-PANi (\% PANi)} = \frac{22.5}{6.25}100 = 360$$

which means that aniline would grow on poly(S-*co*-PAAMS) as well.

Study on results of STA, SEM, and GPC

Thermograms of STA (DSC and TGA) PS-*g*-PANi are illustrated in Figure 1. Comparison of these thermograms with STA thermograms of PS specifies that softening, melting points, and heating resistance of the produced copolymer is higher than when they have not been grafted.

As shown in PS-*g*-PANi thermogram, this polymer at 50°C started to soften, and up to 268.84°C, it lost ~7.628% of it's weight, which is due to humidity and existing solvent or part of the HCl in chains polymer, and by about 485.41°C, it was substantially degraded. PS-*g*-PANi is quite stable below 350°C, and over 360°C, the polymer starts to degrade, which continues to 450°C. The methods of interpreting TGA results are numerous, but lack standardization. Some of these note the temperature of the 5–10% loss, or by the temperature inflection of the down ward slope, or by the first detectable break in the curve. The STA of PS-*g*-PANi illustrated that initial decomposition temperature, polymer decomposition temperature, and the maximum polymer decomposition temperature were 350°C, 400°C, and 480°C, respectively. The residual weight (γ_c) of the polymer is reported as 12.79% at 600°C.

Conductivity measurement

The most important physical properties of conductive polymers is conductivity properties. By increasing the percentage of PANi in PANi/PS weight ratio on graft copolymer, the conductivity increased but its stability decreased a little too. Therefore, we achieved graft polymerization at different PANi

TABLE I
Effect of the PANi Weight Percentage in PS[a]-*g*-PANi on the Conductivity (S cm^{-1}) and Mechanical Properties of the Films

% PANi on copolymer	Conductivity		Mechanical properties
	Before doping	After doping[b]	
120	5.5×10^{-1}	8.3×10^{-2}	Smooth, most flexible
240	9.2×10^{-1}	3.4×10^{-2}	Smooth, flexible
360	3.1×10^{-1}	1.2×10^{-2}	Smooth, flexible
450	8.4×10^{-1}	5.5×10^{-2}	Smooth, slightly brittle

[a] Synthetic polymer.
[b] Doping carried out by 1.5 M HCl Solution after the 1 h.

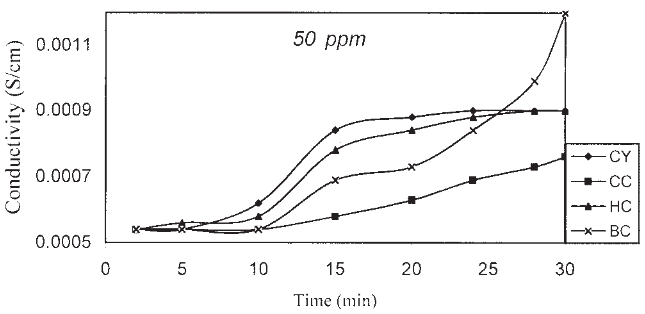


Figure 2 The conductivity changes of PS-*g*-PANi, $\delta_0 = 5.5 \times 10^{-4}$ S cm^{-1}, *versus* time for 50 ppm of CY, CC, HC, and BC at room temperature.

weight percentages on PS, such as 120, 240, 360, and 450, and produced 5.5×10^{-4}, 9.2×10^{-4}, 3.1×10^{-3}, and 8.4×10^{-3} S cm^{-1} conductivity, respectively. The effect of percentage of PANi on properties of the film copolymer is reported in Table I. The best electrical and mechanical properties with different graft percentages of PANi on copolymer are 360 PANi%. The conductance measurements of PS-*g*-PANi film, which is affected by different concentrations of some toxic cyanide compounds (blood agents), are reported in Table II. The resistivity of PS-*g*-PANi decreases upon exposure to tested samples. The conductivity changes, upon exposure to relatively small gas and vapor concentrations were slightly reversible. When higher concentrations of samples were used, the conductivity changes became irreversible. The results in Table II show results of test samples exposed to the produced gases and vapors after 2 min.

Reducing response times of conductive polymers is very important for blood agents. If the concentration of the test samples increases, the conductivity will increase too (see Table II). At constant concentration, by changing doping time, the conductivity increases. In this case, the changes of conductivity of PS-*g*-PANi to doping time at constant concentrations (50, 100, and 150 ppm) of cyanide compounds has been tested. These curves are represented in Figures 2–4.

TABLE II
Conductance Changes PS-*g*-PANi, δ_0, $3.1 \cdot 10^{-3}$ S cm^{-1} for Different of Cyanide Compounds after 2 Min

Relative Concentration (ppm)	50	100	150
HC	3.9×10^{-3}	7.4×10^{-3}	9.7×10^{-3}
CY	4.2×10^{-2}	8.5×10^{-3}	1.2×10^{-2}
CC	3.5×10^{-3}	6.8×10^{-3}	8.1×10^{-3}
BC	4.6×10^{-2}	9.2×10^{-3}	4.6×10^{-2}

CONCLUSIONS

We examined grafting aniline to polymers such as polystyrene (PS), and it's growth on the chains. Creating a conducting copolymer enables study of the grafted polymers for acceptable electronic properties. Although these polymers have low electric conductivity, they easily react to, and show effects against, cyanogens gases. The level of conductivity, before and after doping, relates to the weight ratios of PS/PANi. Conductivity increases with the increasing weight ratio of PANi in graft copolymer. The advantages of this work over our previous works[12,15–18] are their operation at room temperature, decreasing response times, conductance stability over long times to air, sufficient diffusion of gas into the polymer chain, and better reversibility and processibility. The sensing properties of PS-*g*-PANi to cyanide compounds are better than PS-*g*-PPy and PPy. So, PS-*g*-PANi is good candidate for sensing blood agents. The sensing shown in curves (Fig. 2–4) would have been more significant, if we had

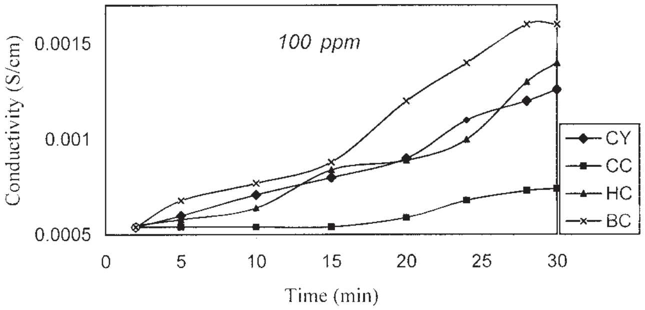


Figure 3 The conductivity changes of PS-*g*-PANi, $\delta_0 = 5.5 \times 10^{-4}$ S cm^{-1}, *versus* time for 100 ppm of CY, CC, HC, and BC at room temperature.

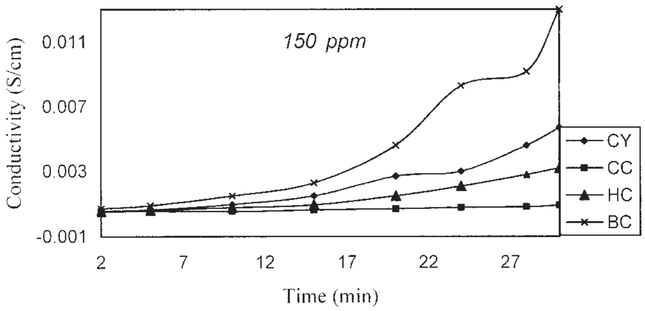


Figure 4 The conductivity changes of PS-*g*-PANi, $\delta_0 = 9.2 \times 10^{-4}$ S cm^{-1}, *versus* time for 150 ppm of CY, CC, HC, and BC at room temperature.

amplified conductivity scale and increased the precision of four-probe device.

References

1. Zhu, D. G.; Cui, D. F.; Harris, M.; Petty, M. C. Sens Actuators B 1993, 12, 111.
2. Wright, J. D.; Roisin, P.; Rigby, G. P.; Nolte, R. J. M.; Thorpe, S. C. Sens Actuators B 1994, 13–14, 276.
3. Vukusic, P. S.; Sambles, J. R. Thin Solid Films 1992, 221, 311.
4. Bartlett, P. N.; Liang-Chung, S. K. Sens Actuators B 1989, 20, 287.
5. Nylander, C.; Armgarth, M.; Lundstrom, I. Anal Chem Symp Ser 1983, 17, 203.
6. Miasik, J.; Hopper, A.; Tofield, B. J Chem Soc Faraday Trans I 1986, 82, 1117.
7. Yoneyama, H.; Hanawa, T. Synth Met 1989, 30, 341.
8. Yoneyama, H.; Hanawa, T.; Huwabata, S.; Hashimoto, H. Synth Met 1989, 30, 173.
9. Hosseini, S. H.; Entezami, A. A. Eur Polym Mater 1995, 31, 7, 635.
10. Crosby, G. A.; Calif, P. A. U.S. Pat. 3,995,094.
11. Hosseini, S. H.; Entezami, A. A. Iranian Polym J 1999, 8, 3, 205.
12. Hosseini, S. H.; Entezami, A. A. Polym Adv Technol 2001, 12, 8, 482.
13. Kondo, S.; Ohtsuka, T.; Ogura, K.; Tsuda, K. J Macromol Sci Chem 1979, A13, 6, 767.
14. Hosseini, S. H.; Entezami, A. A. Polym Adv Technol 2001, 12, 8, 524.
15. Galvin, M. E., Wnek, G. E. Polym Commun 1982, 23, 795.
16. Bates, F. S., Baker, G. L. Macromolecules 1983, 16, 704.
17. Hosseini, S. H. Entezami, A. A. J Appl Polym Sci 2003, 90, 40.
18. Hosseini, S. H.; Ghavami, A. Iranian Polym J 2005, 14, 2, 101.