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Graft Copolymer of Polystyrene and Polypyrrole and Studies of Its Gas and Vapor Sensing Properties

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ABSTRACT

In view of their sensitivity to oxidation and to doping gases, it would seem natural to use conducting polymers as chemical sensors. The first graft copolymer of polypyrrole has been synthesized by chemical and electrochemical polymerization of pyrrole in the presence of poly(*para*-chloromethylstyrene-*co*-styrene-*co*-pyrrolemethylstyrene), which is abbreviated as PCMS-*co*-S-*co*-PMS. Electrochemical synthesis of PCMS-*co*-S-*g*-PPy was carried out in conventional three electrodes system with a SCE reference electrode, platinum wire counter electrode, GC disk working electrode and tetrabutylammonium hexafluorophosphat in acetonitrile as carring electrolyte. The produced copolymer exhibits an electrical conductivity comparable to that of polypyrrole. Then, prepared films were exposed to hydrogen halides, hydrogen cyanide, halogens, 1,3,5-trichloromethyl benzene (TCMB), methylbenzyl bromide (MBB), bromoacetone (BA), and cyanogen bromide (CB). Thermal stability of PCMS-*co*-S-*g*-PPy was investigated by scanning thermal analysis (STA), differential scanning calorimetry (DSC) and thermal gravimetrical analysis (TGA). TGA thermogram of copolymer showed multistep thermal degradation behaviour. This measurement showed that copolymer has excellent thermal stability. The response mechanism of this compound to sense a selection of gases and vapors was investigated, by measuring its electrical conductinty by four-point probe method. This gas sensor may have advantages over the other sensors in its ability to operate at room temperature, lower gas and vapous sensing concentration, suitable solubility, stability in air, sufficient diffusion, and selectivity.

Key Words:
graft copolymer;
conducting polymer;
gas sensor;
conductivity;
polystyrene.

INTRODUCTION

Polypyrrole (PPy) and some of its derivatives have high antioxidative stability and are considered to belong to the most useful conductive polymers for practical application. They can be obtained in various solvents by chemical or electrochemical oxidation. Then by reductive coupling, it is leading to insoluble and infusible powders [1]. Polymers thus obtained are rather difficult to process, therefore it limits considerably their application in industrial technology. One way to bypass these difficulties is to

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prepare blends, composites, or graft of conductive polymers with classic ones, which has the great advantage in improving both their mechanical properties and their processability [2,3].

For the preparation of PPy blends, several methods have been developed. By the copolymerization method pyrrole is grafted onto a polystyrene backbone [4] or onto a PMMA backbone [5]. The composite method involves the inclusion of electrochemically polymerized pyrrole in the matrix of a host polymer. Conducting polymer blends have been obtained by electrochemical polymerization of pyrrole in a poly(urethane) [6], poly(vinyl chloride) [7], or poly(vinyl alcohol) [8] matrix. However, There are limitations in regard to practical applications of polymer composites prepared by electrochemical method. Indeed, for this process, uniform thin films of the host polymers are necessary and they are difficult to prepare on a large scale [9, 10].

Recently Stanke and his coworkers [11] has been reported that graft copolymers from poly(methylmetacrylate) and polypyrrole (PPy) has good amount of conductivity. These graft copolymers have been connected to each other by an ethylene intermediate and they have physical properties and suitable conductivity.

The graft copolymers prepared from hydrophilic polymers, polyvinyl acetate (PVAc) and PPy could be appropriate for various applications in science and technology due to their good mechanical properties and electrical conductivities [12]. The family of PPys can be used for biosensors [13], chemosensors [14], electronic devices [15], and as solid electrolytes in rechargeable batteries [16]. Preliminary investigations for employing these polymers as sensitive materials for gas sensors [17], have been promising and more detailed studies are carring out.

In the previous paper [12] we described the synthesis of polyvinyl acetate grafted polypyrrole (PVAc-*g*-PPy) and, studied its sensing properties for some toxic gases. In this work pyrrole (Py) was grafted by using chemical and electrochemical oxidation, respectively via $FeCl_3$ as oxidant and then with applying sufficient potential. The aim of grafting PPy onto a thermoplastic backbone was to improve solubility and processability of the resulting PPy-containing copolymer.

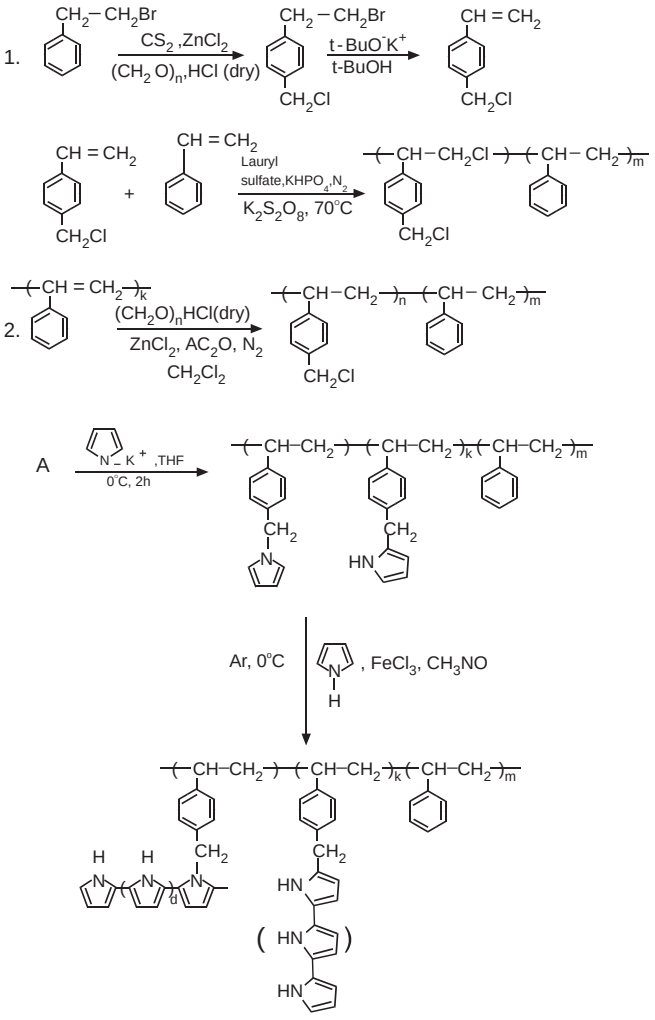
On the other hands, PVAc-*g*-PPy sensing properties were improved by increasing its gas and vapor permeability.

In this work we also studied conducting, thermal, and sensing properties of the grafted copolymer polystyrene (PS) with PPy which were cast onto films, and improved its thermal and sensing behaviours (Scheme I).

EXPERIMENTAL

Instrumentals and Materials

Conductivity changes were measured with four probe device (home made). Elemental analysis was determined with Perkin-Elmer 2400 CHN. A fourier-transform infrared spectrometer (8101 M-Shimadzu) was used in spectral measurements of the polymer and copolymer films. Cyclic voltammetry and electrochem-



Scheme I

ical polymerization were carried out using digital potentiostate DP8 (home made). Furrier transform proton nuclear magnetic resonance (FT-^{1}H NMR) spectra were recorded at 200 and 400 MHz on a Bruker WP 200 SY spectrometer with following order (s=sharp, m=medium, w=wide, sh=shoulder). 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 Perkin Elmer Lambda 15 spectrophotometer. Molecular weights were measured at 30ºC with a gel permeation chromatography (GPC) (Waters Associates, model 150-C). Three styragel packed columns with different pore sizes (10^4-10^6 Å) were used. The mobile phase was tetrahydrofuran (THF) with 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 polymer was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) of 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.

Pyrrole (GPR) was dried with NaOH, fractionally distillated under reduced pressure over sodium or CaH_2. Polystyrene (PS), (Aldrich, Medium molecular weight) was used as matrix polymer. Acetonitrile (Merck) was dried on silicagel and distillated on P_2O_5 in the presence of nitrogen gas. All the other materials and gases used in this work were purchased from Merck and purified , or were prepared by methods given in literatures.

Synthesis of *p*-(2-bromoethyl)benzyl chloride

2-Phenylethyl bromide (70 g, 0.38 mol) was dissolved in 50 ml of carbon disulfide in a 1 liter three-necked round-bottomed flask equipped with a stirrer, gas inlet tube, and a reflux condenser. Anhydrous zinc chloride (11 g) and paraformaldehyde (13 g) were added to the flask in three separate portion during the course of reaction. Hydrogen chloride was bubbled into the reaction mixture the rapid stirring for 20 h at 35-40ºC. The lower phase of the reaction mixture was soluble in water. The organic layer was washed with water, diluted sodium carbonate, and water again. After being dried with anhydrous sodium sulfate, the carbon disulfide was distilled from the product and unreacted 2-phenylethyl bromide was recovered by distillation at pressure of about 1333.2 Pa (10 torr). The product, i.e., a mixture of *o*- and *p*-(2-bromoethyl)benzyl chloride was obtained by distillation at bp 91-94ºC/266.64 Pa (2 torr). The mixture was dissolved in 200 ml of petroleum ether and the solution was chilled overnight in a refrigerator. The remaining liquid was decanted and, the obtained solid was recrystallized twice in 200 ml of petroleum ether. The yield was 39 g (54%); mp 48-50ºC [18]. Gas chromatography of obtained compound showed one peak (Carbowax 20M, 10%, Celite 545, 1 m, 160ºC). The ^{1}H NMR spectrum showed 2.97-3.64 ($-CH_2CH_2Br$), 4.47 ($-CH_2Cl$), and 7.19 ppm (aromatic protons).

Synthesis of *p*-Chloromethylstyrene

A 0.55 g (0.014 mole) portion of potassium metal was carefully added to 25 ml of *tert*-butyl alcohol at 50ºC. After all the metal reacted, the solution was cooled to the room temperature and 3 g (0.013 mole) of *p*-(2-bromoethyl)benzyl chloride was added to the solution. The mixture was stirred at 35ºC for 2 h. Then the reaction mixture was poured into 500 ml of water, extracted with ether, and dried with anhydrous sodium sulfate. Then ether was removed under reduced pressure and the residue was distilled in the presence of *p-tert*-butyl catecohol to give 1.7 g of *p*-chloromethylstyrene, bp 88-90ºC/266.64 Pa (2 Torr) [18]

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

Copolymerization of *p*-chloromethylstyrene and styrene was carried out in a sealed tube at 60ºC. The required amounts of *p*-chloromethylstyrene, comonomer, AIBN, and then benzene as solvent were charged into a pyrex glass tube, which was then degassed under vacuum by conventional freezing and thawing technique and sealed off under vacuum. All copolymers were poured into a large amount of methanol to precipitate the copolymer. The resulting copolymers were then purified by the reprecipitation of the benzene solution with excess methanol. The composition of the copolymer was calculated from its elementary analysis of cholorine, 15.5% (2.17 mmol of Cl/g).

Preparation of Poly(*p*-chloromethylstyrene-*co*-styrene-*co*-pyrrolemethylstyrene) (PCMS-*co*-S-*co*-PMS)

Dissolve 0.62 g PCMS-*co*-S in a 50 mL dry dioxane in 250-mL three-necked flask equiped with a mechanical stirrer, condenser, and a dropping funnel (containing 2.94 g (0.02 mol) potassium pyrrole [19] in 10 mL dry dioxane). For occasional cooling of flask, an ice-water bath was arranged. The potassium pyrrole solution dropwise was added during 30 minutes to the vigorously strring solution at 0°C temperature. Strring continued for further 2 h and then flask temperature increased to near reflux temperature. Filtered and separated solutions transfer to 100 mL iced methanol that acidified with dilute HCl and precipitated PCMS-*co*-S-*co*-PMS, then filtered again and dried in vacuum (total yield 85%).

UV(THF): λ_{max} = 220 nm (5.5 intensity), 275 nm (2.6 intensity), 361 nm (0.77 intensity), 512 nm (0.72 intensity)

ATR(film): ν = 3050(m), 3030(sh), 2930(m), 1620(s), 1550(m), 1455(m), 1410(sh), 1200(m), 1100(s), 990(m), 780(w), 706(m) cm^{-1}

FT-^{1}H NMR (d_6-DMSO): δ = 6-7.5(m,broad,12H), 4.78(s,sharp,2H), 4.02(s,sharp,1H), 1.56 (s,broad,2H) ppm

Chemical Preparation of Poly[(*p*-chloromethylstyrene-co-styrene)-*g*-polypyrrole] (PCMS-*co*-S-*g*-PPy)

Prepared a solution of 0.5 (4.0 10^{-4} M) g (PCMS-*co*-S-*co*-PMS) in 20 mL nitromethane in a two-necked, 250 mL round bottom flask fitted with a dropping funnel under N_2 atmosphere. Insert a plastic-covered magnetic stirrer follower bar and cool the flask in an ice bath sited on the stirrer unit. To the cooled and stirred solution add 135.5 mg (8.58 10^{-4} M) of anhydrous ferric chloride in 10 mL nitromethane. Then 3.8 10^{-2} g (5.6 10^{-4} M) pyrrole was added dropwise to the stirring solution. This solution filtered after 30 minute and precipitated in iced methanol containing 5% HCl. Then refiltered with G3 sintered glass funnel and washed with iced methanol and water few time. Black percipate dried in vacuum. The molar ratio of $FeCl_3$/pyrrole was chosen 3/2 because it led to yield high, conductive copolymer.

UV(THF): λ_{max} = 225 nm (5.1 intensity), 260 nm (1.6 intensity), 320.6 nm (4.2 intensity), 360 nm (1.1 intensity)

ATR (film): ν = 3030(m), 2937(sh), 2860(sh), 1950(m), 1811(m), 1750(s), 1611(m), 1503(m), 1455(m), 1400(m), 1117(m), 950(m), 700(w), 623(w) cm^{-1}

FT-^{1}H NMR (d_6-DMSO): δ = 8.12(s,broad,4H), 6-7.5(m,broad,18H), 4.78(s,sharp,2H), 4.11(s,sharp,1H), 1.49(s,broad,2H) ppm

Electrochemical Preparation of PCMS-*co*-S-*g*-PPy

Electrochemical synthesis of (PCMS-*co*-S-*g*-PPy) was carried out using a conventional three electrodes system with a SCE reference electode, 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 stored over molecular sieves.

Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was bubled by dry and oxygen free, nitrogen stream for at least 20 minutes before each cyclicvoltammetry. Firstly coated a suitable amount of PCMS-*co*-S-*co*-PMS on GC disk electrode by using casting method and then add various amount of pyrrole. The polymer was growning on GC disk electrode under scan potential range of -450 – +1700 μmV and scan rate of 50 mV/s. The thickness of the film was ca. 20 m as determined by scanning electron microscopy in 1/1 weight ratio of PCMS-*co*-S / Py.

Preparation of PCMS-*co*-S-*g*-PPy Film

0.1 gram of PCMS-*co*-S-*g*-PPy black powder was slowly added (over 30 min) to 20 mL of nitromethane or nitrobenzene solution and stirred magnetically at room temperature for 5 h. The resulting low viscous solution was pre-filtered twice in vacuum, through a Buchner funnel using Whatman paper No. 541 to remove its particles. The produced low viscous solution of polymer was spread over a piece of glass to obtain an even layer, then dried under vacuum. In general, slowly drying makes the tickness of the film more uniform. Dried film was removed from the glass by immersion in water. The film prepared from 8 mL of solution casted over a piece of glass (2 2 cm) gave a film with thickness of ~ 30-35 μm. Conductivity of the polymer film measured with four-point probe method,

and obtained 1.2 10^{-3} S/cm.

Sensor Fabrication and Toxic Gas-vapor Generation Apparatus

The polymer film prepared in this manner, was fabricated for testing the gases sensitivity [17]. For this purpose, the prepared film fixed onto a glass plate by 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 [17,20,21]. However the method of gas and vapor generation was different. A system was designed consisting of a series of needle valves, for controlling gas flow rates, which 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}. Testing gas and vapor flows, adjustable from 1 to 20 cm^3 min^{-1}, were mixed with the argon carrier flows. So by controlling both gas and vapor flows, different dilutions could be made. Target samples were produced in two ways. Organic vapor were generated by bubbling a stream of argon carrier gas (via gas wash bottles) through the volatile liquids and solids such as HBr, HI, I_2, 1,3,5-trichloromethyl benzene (TCMB), bromoacetone (BA) and methylbenzyl bromide (MBB). Thus produced a continiouse flow of saturated vapor, which its concentration depended on the vapor pressure of the volatile liquids or solids. Analyte samples that are normally in gaseous state at room temperature, were prepared by diluting each of HCN, HCl, Cl_2, Br_2, and cyanogen bromide (CB) with 99.8% purity.

Experimental Procedure

In the preceding works [19,21], we should preswell all polymer films by suitable reagents, like diluted basic and acidic solutions or volatile organic solutions and then heated at 70ºC in 5 mmHg pressure to desorb the residual solvents and humidity out of the polymer films, which could modify the mass and electrical measurements. As this copolymer have good penetrability to gases and vapors. So the sample s temperature was regulated at 20ºC and a constant flow of pure argon (100 mL min^{-1}) is established through the cell. All samples were exposed to Ar atmosphere within the concentration range of 200-2000 ppm when they were transferred from the preparation unit to the measurement equipment. Vapours and gases were sufficiently dry (moisture$\leq$0.6 ppm) to carry out dry experiments on samples. Curves of low concentration of samples during conductivity measurements were generated by allowing a stream of Ar gas, into which gas and vapor samples were injected, passed over the film. The amounts of gases and vapours were regulated by a magnetic valve and a high-percision flow regulator. Conductivity was measured using four-point probe technique. Target gases and vapours exposure were carried out with the film still mounted on the probe.

RESULTS AND DISCUSSION

Measurement of PPy Percentage in (PCMS-*co*-S-*g*-PPy)

In order to assess the percentage of involved polymers in produced mixture we used elemental analysis. Assessing the percentage of the produced mixture was so important because in this way we were able to analyze the quantity and quality of condition of electron conductivity in the produced mixture's properties. In all the mixtures, we made changes in factors such as: density of oxidant, solvent, density of monomers, and polypyroll percentage in polymer. Because we were intended to get the acceptable condition in order to use it in sensitivity measurment. For this reason we studied elemental analysis on reliable films in view of electrical conductivity, stability, and mechanical properties. Since provided polymers based on PPy and PS on the other hands, are without nitrogen atom, so by measuring the percentage of nitrogen in elemental analysis we can achieve the percentage of PPy in copolymer. For assessing the PPy percentage in copolymer we used the following equation. In beginning we measured percentage of theoretical mass of nitrogen in each monomer unit or base polymer PCMS-*co*-S-*co*-PMS.

So, by elemental analysis the introduced nitrogen percentage is 0.61. Therefore percentage of grafted PPy is 35.33.

Results of Cyclic Voltammetry

Cyclic voltammograms of graft electro polymerization of pyrrole to PCMS-*co*-S-*co*-PMS and it s blank in the above condition showed in Figures 1 and 2, respectively. As it is shown in Figure 1 the oxidation peaks of pyr-

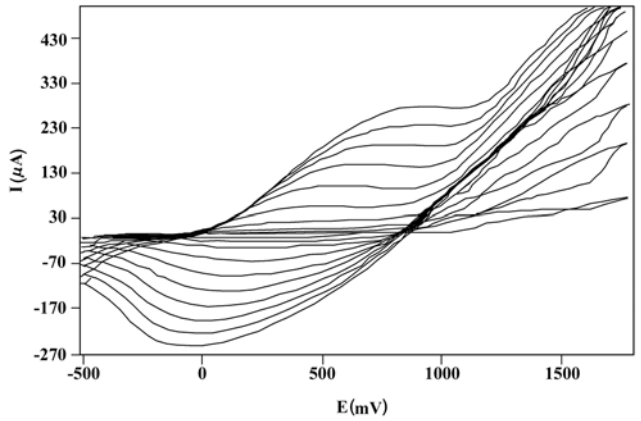


Figure 1. Cyclic voltammograms of formation of styrene-pyrrole graft copolymer on a supporting polymer (PCMS-*co*-S-*co*-MPS), in acetonitrile, 0.1 M Bu_4NPF_6, GC disk electrode vs. SCE, scan rate=50 mV/s (10 cycles).

role monomers on main chain and pyrrole s monomers which are inside the solution have been appeared above +1700 mV, with the 50 mV/s scan rate.

In the next curves gradually, the intensity of oxidation peaks have been decreased and those reduction and oxidation peaks of grafted polymer which are appeared in order, in +50 mV and +800 mV, grow in direct proportion as in Figure 1. Cyclic voltammogram of graft copolymer of PCMS-*co*-S-*g*-PPy illustrates in Figure 2. The oxidation-reduction potentials of this copolymer is different with it's homopolymer. Therefore, cyclic voltammograms confirm the formation of copolymer. Spectroscopy data certify the formation of copolymer at the chemical polymerization, too. As it is shown in voltammogram, PCMS-*co*-S-*g*-PPy has suitable reversibility and well stability on electrode's surface. Figure 3 shows the anodic (ipa) and cathodic (ipc) currents peaks via different scan rate (SCE reference electrode) of PCMS-*co*-S-*g*-PPy. The curves are linear, therefore, the polymers are stable on the electrode surface and the redox reaction of polymer film on electrode surface is of the type of surface absorption. Therefore, we achieved graft electropolymerization in different weight of PCMS-*co*-S/Py ratio such as 1/20, 1/10, and 1/1 and produced conductivity of 0.1, 4.5 10^{-2} and 5.6 10^{-3} S/cm, respectively. We would have had sufficient precipitate on the working electrode with 1/5 weight ratio of (PCMS-*co*-S)/Py.

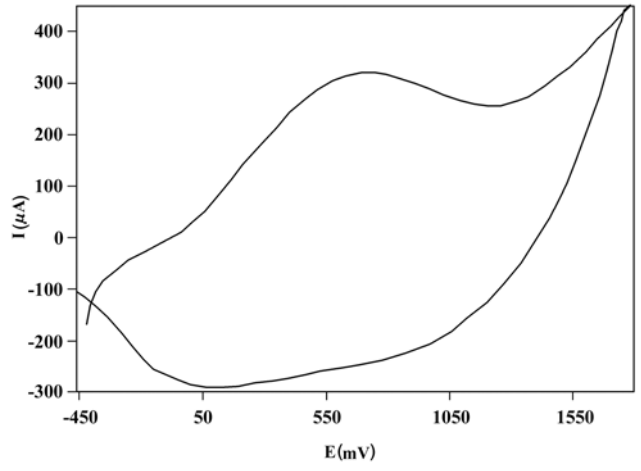


Figure 2. Cyclic voltammograms of PCMS-*co*-S-*g*-PPy (with 24wt. % PPy, (δ) = 5.2×10^{-3} S/cm), in acetonitrile, 0.1 M Bu_4NPF_6, GC disk electrode vs. SCE, (scan rate) = 50 mV/s.

Results of STA, SEM, and GPC

Thermograms of STA (DSC and TGA) of PCMS-*co*-S-*g*-PPy are illustrated in Figure 4. 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 it hasn t been grafted.

As it is shown in PCMS-*co*-S-*g*-PPy thermogram, this polymer in 50°C started to become soften and up to 255.95°C, it approximately losses 6.6% of it s weight which is due to humidity and existing solvent or part of HCl in chains polymer, and in about 430°C it approximately degredates. PCMS-*co*-S-*g*-PPy is stable well below 390°C and in 390°C the polymer starts it's complete distraction which continues to 490°C.

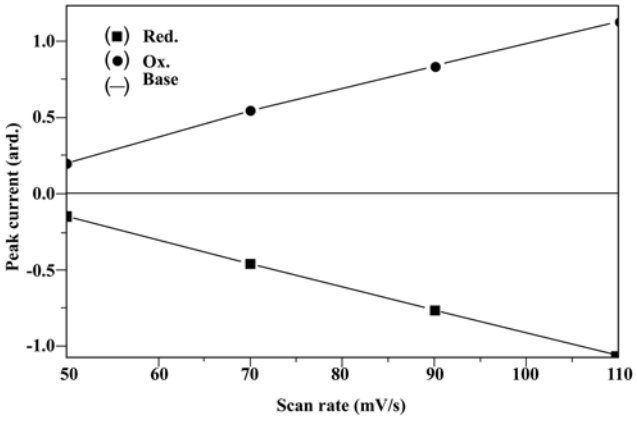


Figure 3. The anodic and cathodic current peak vs. scan rate of PCMS-*co*-S-*g*-PPy.

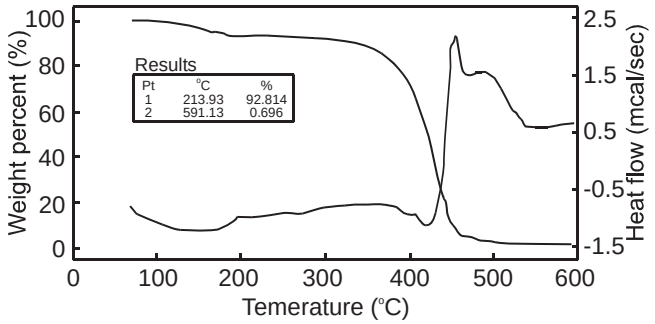


Figure 4. STA (DSC and TGA) Thermmograms of PCMS-*co*-S-*g*-PPy.

Figure 5 shows the image of SEM of PCMS-*co*-S-*g*-PPy. As it is shown in this Figure, monotony and single phase of polymers completely clear and pyrrole's granulate particles in polymer's surface has been grown well and monotony. PPy shows a sponge-like morphology in contrast to PCMS-*co*-S-*g*-PPy which have smooth surfaces indicating that no morphological characteristics could be observed.

Earlier studies on the surface morphology of PS and PCMS-*co*-S have demonstrated theirs smooth surfaces. Despite the fact that PCMS-*co*-S-*g*-PPy contained about 35.33 wt% PPy, according to elemental analysis determination, no free PPy is seen in SEM picture of the graft copolymer. This observation enforces the assumption that covalent bonds between PCMS-*co*-S and PPy chains have been produced.

The GPC of PCMS-*co*-S-*g*-PPy was analyzed using polystyrene standard. The GPC curves obtained, show a unimodal distribution. The molecular weight distribution averages for the polymer is presented in Table 1.

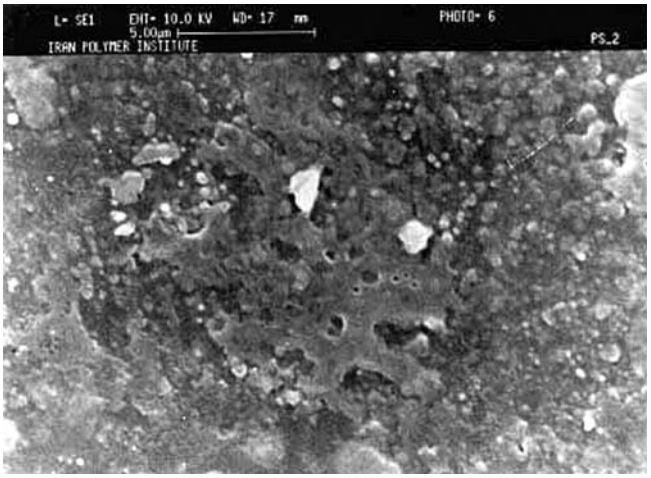


Figure 5. SEM Micrograph of PCMS-*co*-S-*g*-PPy.

Table 1. The molecular weight distribution averages (GPC) for the PCMS-co-S-*g*-PPy.

Molecular weight data	PCMS-*co*-S-*g*-PPy
Number average	32941
Weight average	95703
Z average	212326
Z+1 average	344497
Polydispersity	2.9
Moleculer wt.	71119

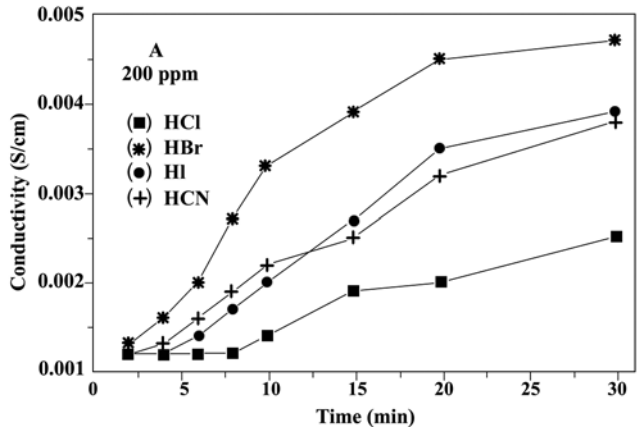
Conductivity Measurement

The conductivity measurement of PCMS-*co*-S-*g*-PPy film which is affected by different concentrations of toxic gases and vapors was reported in Table 2. The resistivity of PCMS-*co*-S-*g*-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 were used, the conductivity changes become smaller and partly irreversible. The results that are shown in Table 2 are those test samples that have been exposed to produced gases and vapors for 10-20 min.

Reducing response times of conductive polymers is very important to toxic gases sensing. If the concentration of the test samples were increased; the conductiv-

Table 2. Conductance changes of PCMS-*co*-S-*g*-PPy, δ_0= 1.2×10^{-3} S/cm for different toxic gases and vapors.

Relative concentration (ppm)	200	400	600
Cl_2	1.6×10^{-3}	1.8×10^{-3}	2.5×10^{-3}
Br_2	2.1×10^{-3}	2.5×10^{-3}	4.2×10^{-3}
I_2	2.8×10^{-3}	4.5×10^{-3}	6.6×10^{-3}
HCl	2.0×10^{-3}	3.1×10^{-3}	3.5×10^{-3}
HBr	3.5×10^{-3}	3.9×10^{-3}	4.5×10^{-3}
HI	4.5×10^{-3}	4.7×10^{-3}	5.5×10^{-3}
HCN	3.2×10^{-3}	3.9×10^{-3}	4.7×10^{-3}
BA	1.4×10^{-3}	1.9×10^{-3}	2.4×10^{-3}
CB	1.6×10^{-3}	2.2×10^{-3}	3.2×10^{-3}
TCMB	5.9×10^{-3}	6.9×10^{-3}	8.1×10^{-3}
MBB	4.3×10^{-3}	6.4×10^{-3}	6.6×10^{-3}



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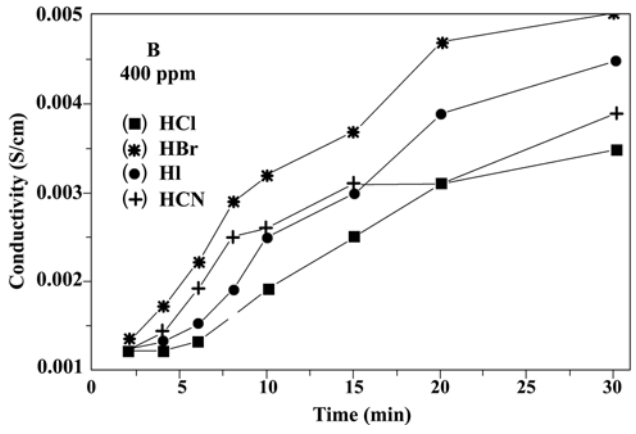

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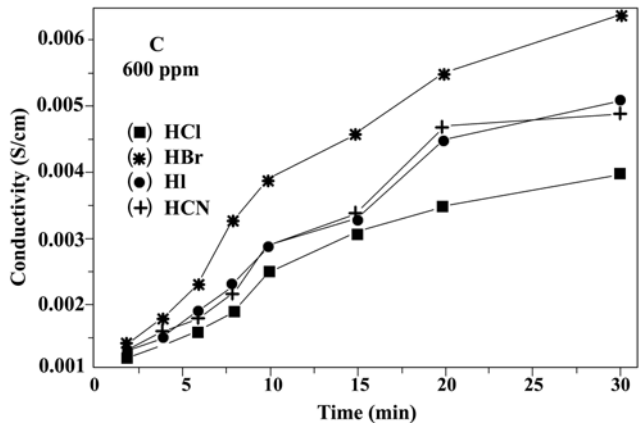
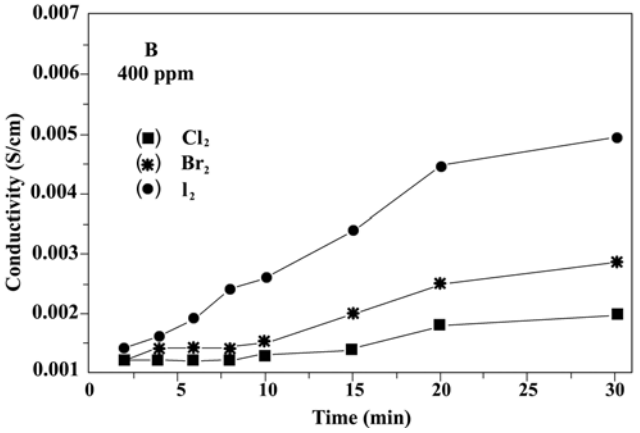


(c)

Figure 6. The conductivity changes of PCMS-*co*-S-*g*-PPy, (δ) = 0.0012 S/cm vs. time for A)200, B)400 and C)600 ppm of HCl, HBr, HI and HCN at room temperature.



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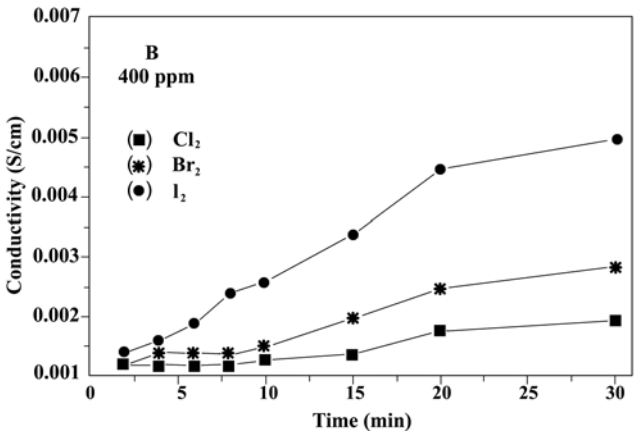

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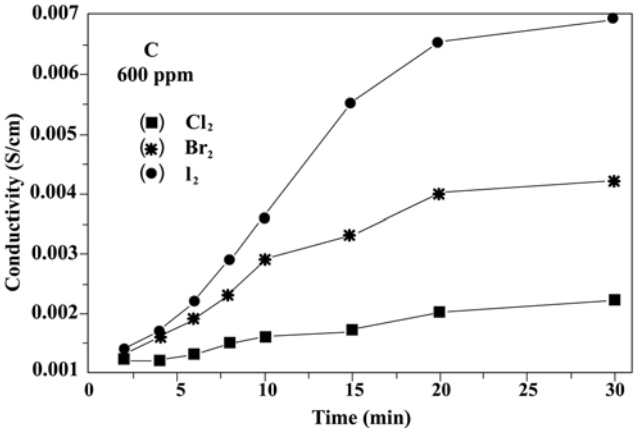
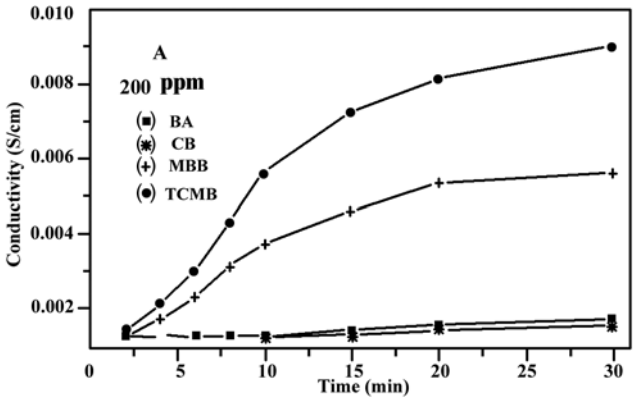


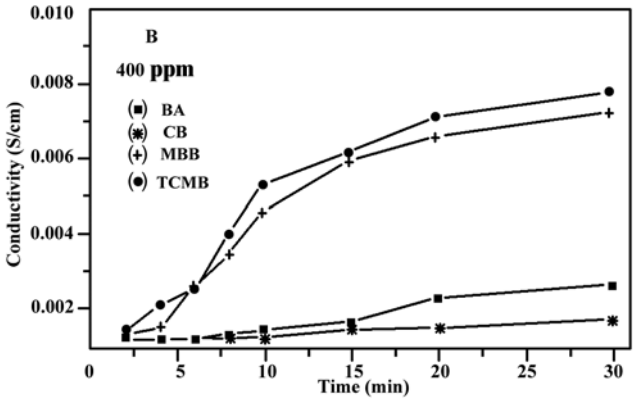
(c)

Figure 7. The conductivity changes of PCMS-*co*-S-*g*-PPy, (δ) = 0.0012 S/cm vs. time for A)200, B)400 and C)600 ppm of Cl_2, Br_2 and I_2 at room temperature.

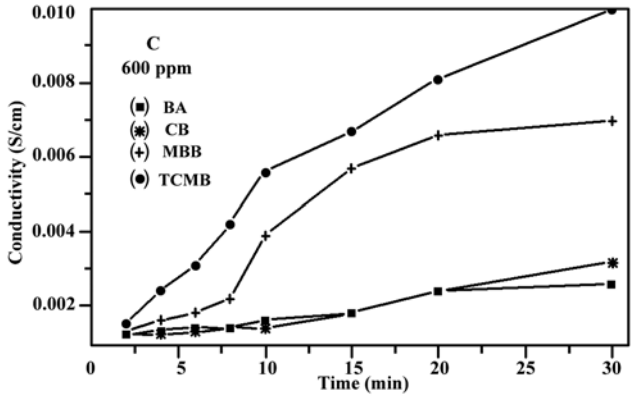
ity would be increase (Table 2). In the constant concentration with changing doping time, the conductivity was increasing. In this case, we plott conductivity changes of PCMS-*co*-S-*g*-PPy versus doping time in



(a)



(b)



(c)

Figure 8. The conductivity changes of PCMS-*co*-S-*g*-PPy, (δ) = 0.0012 S/cm vs. time for A)200, B)400 and C)600 ppm of BA, CB, MBB and TCMB at room temperature.

constant concentrations (i.e., 200, 500, and 800 ppm) of tested gases and vapors. These curves are represented in Figure 6-8. Table 3 shows the effect of mole ratios of

Table 3. Effect of the molar ratio of $FeCl_3$/Py on the conductivity (S/cm) and properties of the films in THF solvent.

Molar ratio of $FeCl_3$/py	Conductivity of PCMS-*co*-S-*g*-PPy	Remarks on the films
1/1	7.3×10^{-3}	smooth, slightly brittle, strong
2/1	9.9×10^{-3}	smooth, flexible, most strong
3/1	9.1×10^{-3}	smoothless, brittle, strong
2/2	7.5×10^{-3}	smooth, slightly brittle, strong
3/2	1.2×10^{-3}	smooth, flexible, strong
4/2	9.0×10^{-3}	smooth, flexible, most strong
5/2	8.5×10^{-3}	smoothless, slightly brittle, strong

$FeCl_3$/pyrrole on conductivity. There is an optimum mole ratio of oxidant ($FeCl_3$) to pyrrole as in 3/2.

The conductivity of PCMS-*co*-S-*g*-PPy increase rapidly with increasing amounts of oxidant below the optimum value, and decreased with a further increase in the oxidant mole ratio. The decrease of the conductivity beyond the maximum is probably due to decrease in the average degree of polymerization. This implies shorter conjugation lengths.

CONCLUSION

Graft copolymer films of PS and PPy were homogeneous due to the chemical bonding between the polymers. The quality of the films, especially their conductivities, depended on several effects which were connected in a complex manner. Graft copolymer films with the highest conductivities of about 1.2 10^{-3} S/cm were obtained using a $FeCl_3$/pyrrole ratio of 3/2. In comparison to pure PPy, their conductivity was lowered by two order of magnitude due to the presence of the N-alkylpyrrole moiety and by an addition three order of magnitude due to the presence of the insulating PCMS-*co*-S matrix. For this reason PCMS-*co*-S/PPy reached a maximum conductivity of 0.11 S/cm due to peneteration and surface absorbtion of toxic gases, but its homogeneity was rather low.

The quality of the graft copolymer films depended on several factors, such as: composition, average graft sequence length, structure defects, and morphology. We must consider all these factoes for suitable behav-

iours and special applications. They must be optimized for different conditions. The average sequence length of the graft was controlled by the PCMS-*co*-S/Py mole ratio in the reaction mixture. Athough long py sequences are more conductive than short ones but decreases its solubility.

Results of studying this polymer show that it has well stable conductivity and nearly high resistance against factors such as air atmosphere, humidity, and etc., but primary changes in its conduction is low. Experience shows that by adding ethylenic spacer between grafted branch and base polymer, as we add more pyrroles to backbone copolymer, polymers conduction and also doping situation increase, and thus the polymer's sensitivity properties can be increased. Conducting graft copolymers don t need to pre-swelling so elimination of this step increase the speed of diffusion of gas in to polymer. The produced results show that PCMS-*co*-S-*g*-PPy is a suitable candidate for detection of aromatic halomethyl compounds and halogens. In future, we will intend to improve sensing effects with aniline in replace of Py.

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