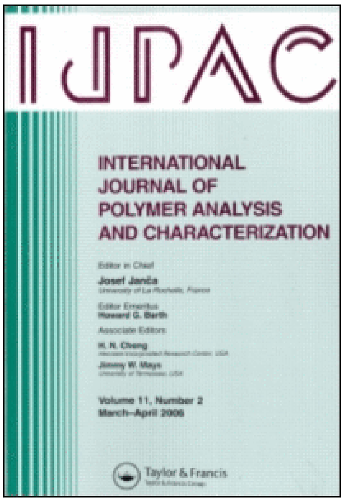

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Conducting Polyaniline Sensors for Some Organic and Inorganic Solvents

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Conducting Polyaniline Sensors for Some Organic and Inorganic Solvents

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Abstract: Polyaniline (PAn) emeraldine salts (PAn-Cl, PAn-Br, PAn-ClO_4) were synthesized by the electrochemical method using different acids (HCl, HBr, $HClO_4$). PAn salts in pellet form were used as sensors for organic (EtOH, $CHCl_3$, C_6H_6) and inorganic (HCl, NH_3) solvents. Electrical conductivity responses of PAns to five solvents were investigated. The change of electrical conductivity of PAns ($\Delta\sigma$), relative to the value measured before exposure, varied with the solvent used. The sensor properties of PAns varied depending on the nature of dopant anions such as the type and size. It was found that PAn-ClO_4 has the highest sensing power on HCl, NH_3, and $CHCl_3$, and it has the lowest sensing power on C_6H_6.

Keywords: Conductivity; Organic and inorganic solvents; Polyaniline; Sensor

INTRODUCTION

Increased interest in environmental protection has led to a continuous expansion in sensor development. A sensor is a transducer that converts

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one form of energy into another form suitable for further processing. Although sensors of a great variety of types are well established in process industries, agriculture, medicine, and many other areas, the development of sensing material with high sensing capabilities is proceeding at an unprecedented rate. Numerous materials have been utilized as humidity, organic, and inorganic vapor sensors. Metal oxides that are physically and chemically stable have been extensively investigated.[1–4]

In general, metal oxides have good chemical and thermal stability. Sensors based on changes in resistance and capacitance are preferred to conventional ones owing to their compact size, which could facilitate miniaturization required for electronic circuitry. The high surface area, size, hollow geometry, and chemical inertness, the remarkable properties of carbon nanotubes (CNTs) and composites based on CNTs, make them attractive in applications as sensors for inorganic vapors.[5]

Electrically conducting polymers have been widely investigated as effective materials for chemical sensors.[6–10] Conducting polymers have recently gained popularity as valuable sensing materials for various organic vapors,[11] hazardous gases,[12] and humidity,[13] and as a fabricating material for sensor devices because of their applicability at room temperature. Many conducting polymers have shown changes in resistivity on exposure to different gases and humidity. Among the members of this family, polyaniline (PAn) is promising for its ease of preparation, high environmental stability, stable electrical conduction mechanism, and special properties.[14–16]

Conducting polyaniline has been used as a sensing material for different vapors like methanol, ethanol, acetone, and benzene.[17,18] The effect of these vapors on the electronic properties of PAn has been investigated.[19] Conducting polymers generally show highly reversible redox behavior with a distinguishable chemical memory and hence have been considered as prominent new materials for the fabrication of industrial sensors. The properties of conducting polymers depend strongly on the doping level, ion size of dopant, protonation level, and water content.

Conducting polyaniline is prepared either by electrochemical oxidative polymerization or by the chemical oxidative polymerization method. The emeraldine base form of polyaniline is an electrical insulator consisting of two amine nitrogen atoms followed by two imine nitrogen atoms. Polyaniline emeraldine base can be converted into a conducting form by two different doping processes: protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base corresponds to the protonation of the imine nitrogen atoms in which there is no electron exchange. In oxidative doping, emeraldine salt is obtained from leucoemeraldine through electron exchanges. The mechanism causing the structural changes is mainly attributed to the presence of –NH group in the polymer backbone, whose protonation and deprotonation will bring about a change in the electrical conductivity as well as in the color of the polymer. Considerable research effort is now directed towards the development of sensors and artificial noses and tongues based on conducting materials used for the recognition of chemical vapors and gases and biological species.[20] It has been found that when these films are exposed to electron-donating gases such as ammonia, their absorption will cause an increase in resistance, while an increase in conductivity is observed with gases such as HCl and H_2SO_4. Nevertheless, the application of polyaniline as a sensor for vapors of chlorinated hydrocarbon solvents has been less investigated, probably because of their weak interactions. Electrochemical polymerization provides homogeneous electrical conductivity across the surface area of polyaniline. Furthermore, the product is purer than that obtained by the chemical method. For this reason, we used the electrochemical method to synthesize polyanilines in the presence of different acids such as HCl, HBr, and $HClO_4$. The conductivity of these polymers can be varied by doping them with different protonic acids or functionalized protonic acids. The possibility of synthesizing polyaniline with protonic acid dopants containing different types of counterions is one of the key factors responsible for the versatility of this class of polymers. We investigated the sensors based on PAn salts synthesized using different acids and sensitive to the vapors of various solvents.

EXPERIMENTAL SECTION

Materials

The aniline, purchased from Aldrich, was distilled prior to use. Hydrochloric acid (HCl), hydrobromic acid (HBr), perchloric acid ($HClO_4$), ammonia, chloroform, ethanol, and benzene were purchased from Merck and used as received.

Synthesis of PAn-Cl, PAn-Br, PAn-ClO_4

PAns were synthesized by the electrochemical method described by Trivedi[21] by using a Wenking VSG 83 model potentiostat-galvonastat system at constant potential. Syntheses were carried out in a three-compartment cell, one each for working, counter, and reference saturated calomel electrodes. The surface areas (2.5 cm^2) of platinum working and counter electrodes were the same for the electrolysis experiments. The 0.1 M aniline and 0.2 M acid solutions (HCl, HBr, $HClO_4$) were electrolyzed at constant potential and room temperature. The polymer was obtained as a powder and dried in a vacuum oven at 70°C for 24 h.

Conductivity Measurements

The polymer powder samples were pressed into pellets of 13 × 2.5 mm dimension with 4 t pressure in a hydraulic press. Their conductivities were measured at room temperature employing the four-probe technique (Nippon, Osaka, Japan). The sensing performance of the PAns was tested by subjecting the PAns pellets to saturated vapors of solvents, i.e., HCl, NH_3, chloroform, ethanol, and benzene, for the same periods at room temperature. The sensing measurements were performed by exposing the sensor (pellets) alternately to vapors in a closed glass container held at a distance of 1 cm. The contacts were made with the help of a silver probe and the change in resistance was measured using a four-probe method.

RESULTS AND DISCUSSION

The electrochemical polymerization of aniline proceeds through the formation of a radical cation initiated by electrolysis and follows the mechanism reported earlier.[22] During the course of polymerization reaction, these cations of intermediate stability dimerize, and further radical coupling reaction leads to the formation of green polyaniline, as shown in Scheme 1.

The properties of polyaniline vary with the nature of the dopant anion because the protonation in PAn involves ingression of anions so as to maintain charge neutrality along the whole polymer backbone. PAns synthesized using three different acids show various conductivity values.

The conductivity data given in Table I yield the following order of increase in conductivity:

$$\text{PAn-Cl} < \text{PAn-Br} < \text{PAn-ClO}_4$$

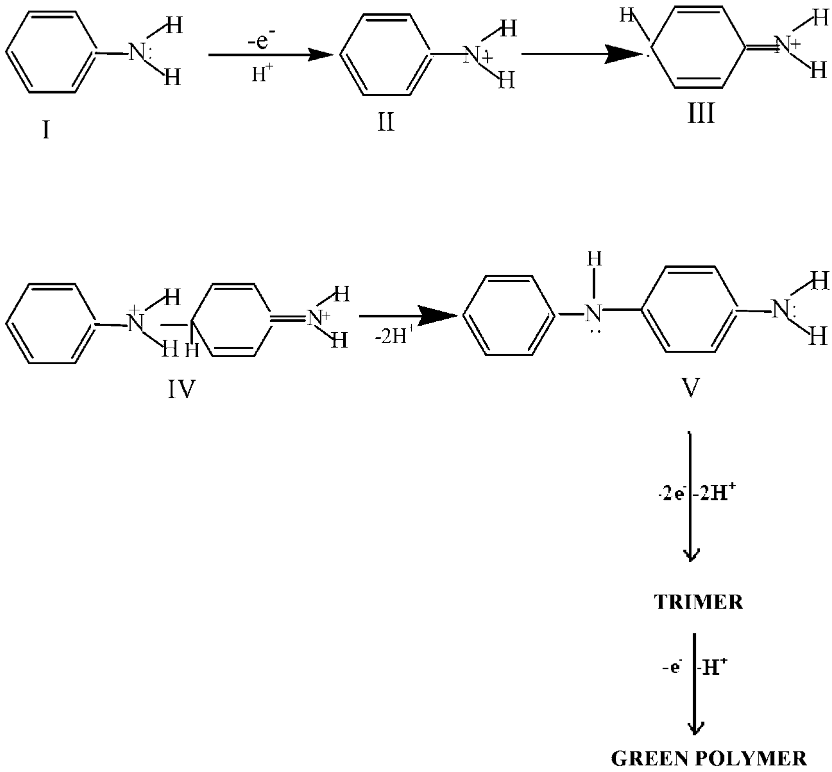
This trend is quite understandable when considering the role of the dopant in the polymer material. Table I lists the conductivity values of native (σ_R) and solvent-vapor exposed (σ_s) PAn salts together with reduction and percentage conductivity change (ppc).

$$(\text{pcc} = [(\sigma_s) - (\sigma_R)/\sigma_R] \times 100)\ \text{due to solvent}^{[23]}$$

The magnitude of conductivity change (maximum pcc given in parentheses) is found to be in the following decreasing order:

$$\underset{(90.9)}{\text{PAn-ClO}_4} > \underset{(71.0)}{\text{PAn-Br}} > \underset{(54.3)}{\text{PAn-Cl}}$$

which coincides with the decreasing order of native conducting (σ_R) of the these materials (Table I). A comparison of the magnitude of conductivity



Scheme 1. Growth mechanism of aniline to polyaniline.

Table I. Effect of solvent vapor on conductivity of PAns

		Solvent exposed (σ_s) (Scm^{-1})				
Material	Reference (σ_R) (Scm^{-1})	HCl (37.0%)	NH_3 (30.0%)	$CHCl_3$ (99.8%)	EtOH (97.0%)	C_6H_6 (99.8%)
PAn-Cl	0.35	0.37	0.19	0.30	0.16	0.16
($\sigma_s - \sigma_R$)		0.02	−0.16	−0.05	−0.19	−0.19
pcc		5.71	−45.7	−14.3	−54.3	−54.3
PAn-Br	0.69	0.80	0.50	0.20	0.80	0.21
($\sigma_s - \sigma_R$)		0.11	−0.19	−0.49	0.11	−0.48
pcc		15.9	−27.5	−71.0	15.9	−69.6
PAn-ClO_4	1.10	2.00	0.10	0.10	0.85	1.0
($\sigma_s - \sigma_R$)		0.9	−1.00	−1.00	−0.25	−0.10
pcc		81.8	−90.9	−90.9	−22.7	9.09

Exposure time = 10 min.

Table II. The ppc increase in PAns

PAn-Cl: $HCl < CHCl_3 < NH_3 < EtOH \cong C_6H_6$
PAn-Br: $EtOH \cong HCl < NH_3 < C_6H_6 < CHCl_3$
PAn-ClO_4: $C_6H_6 < EtOH < HCl < CHCl_3 \cong NH_3$

change ($\Delta\sigma$) between the on-off cycles for different solvents revealed that PAn-ClO_4 shows both the highest positive and negative change. As seen from Table I, each solvent has a different characteristic effect on the conductivity of PAns. $CHCl_3$ has considerable effect on PAn-Br and PAn-ClO_4, whereas it has small effect on PAn-Cl. In contrast to PAn-ClO_4 and PAn-Br, PAn-Cl has the highest sensing power on EtOH. Similarly, the pcc values of PAn-ClO_4 exposed HCl and NH_3 solvents are higher than those of PAn-Cl and PAn-Br. The sensitivity was found to be greater than 80% for PAn-ClO_4 towards inorganic vapors. It decreased in the case of $CHCl_3$ and benzene vapors. Hence, it has been concluded that PAn-ClO_4 can be used as sensor material for the detection of inorganic acids vapors. Summarizing, it can be said that the sensing behavior is not identical for PAns but exhibits specificity. Although the measurement time is long, the conductivity changes are sensitive and reversible.We have shown the specificity in the order of PAns and solvents with increase in pcc (Tables II and III).

PAns synthesized using three different acids were studied as sensors for saturated vapors of a number of solvents. It has been observed that all polymers respond to different solvent vapors. Differences related to the rapidity, reproducibility, and sensitivity of these polymers towards each of these solvents were observed. Many authors attribute the response of polymer sensors to volatile vapors in terms of the fractional resistance change, $\Delta\sigma/\sigma_R$, of the sensor. This can be defined as

$$\frac{\Delta\sigma}{\sigma} = \left(\frac{\sigma - \sigma_R}{\sigma_R}\right)$$

where σ is maximum (minimum) conductivity of the sensor following exposure to the vapors and σ_R is the initial conductivity. Figures 1 to 5 show the typical response curves ($\Delta\sigma/\sigma_R$-time) for the PAn series exposed

Table III. The ppc increase in solvents

HCl: PAn-ClO_4 > PAn-Br > PAn-Cl
$CHCl_3$: PAn-ClO_4 > PAn-Br > PAn-Cl
C_6H_6: PAn-Br > PAn-Cl > PAn-ClO_4
NH_3: PAn-ClO_4 > PAn-Cl > PAn-Br
EtOH: PAn-Cl > PAn-ClO_4 > PAn-Br

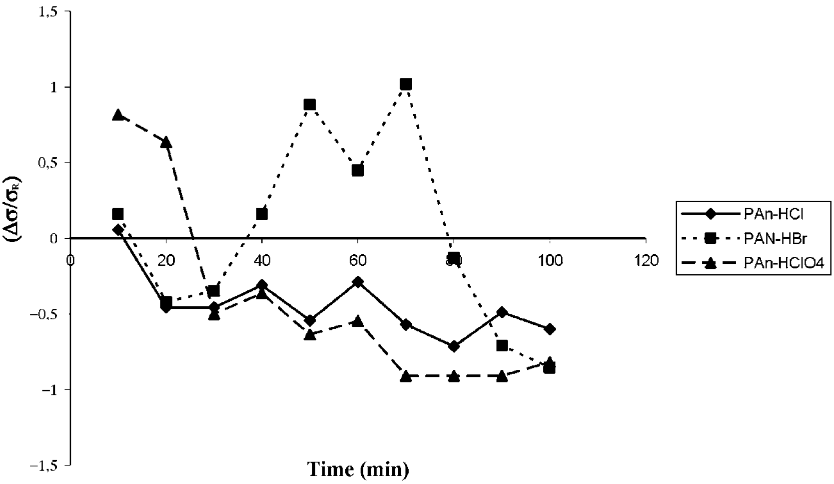


Figure 1. Changes of the electrical conductivity of PAns exposed to HCl.

to saturated vapors of hydrochloric acid, ammonia, chloroform, ethanol, and benzene, respectively. As can be seen from the figures, the conductivities of polymers show marked changes when exposed to different solvents. The change in conductivity of polymers can be attributed to the different nature of both dopant anions and solvents. Dopant anions have different sizes and solvent vapors can differently diffuse in polymer matrix. Moreover, the solvents exhibit various characteristic properties.

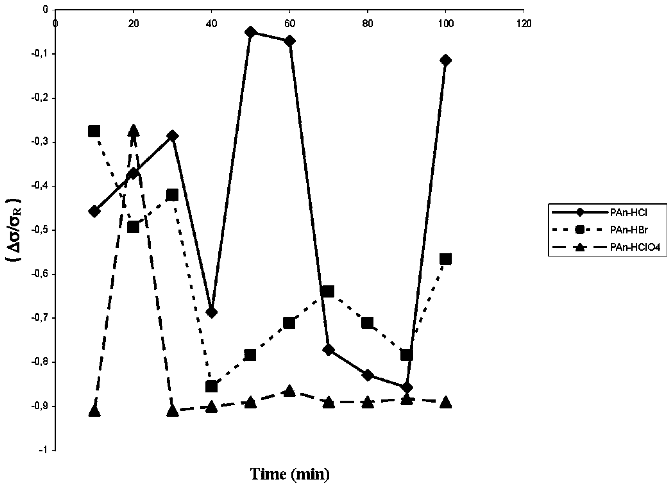


Figure 2. Changes of the electrical conductivity of PAns exposed to NH_3.

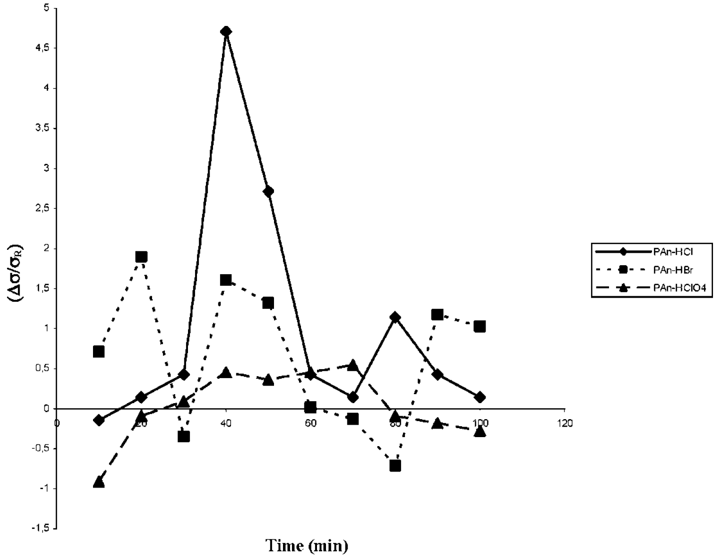


Figure 3. Changes of the electrical conductivity of PAns exposed to $CHCl_3$.

As can be seen from Figure 1, the conductivity change of PAn-ClO_4 increased on first exposure to HCl vapor. The reason for the increase may be the protonation depending on Cl^- anion. But, on successive exposure, this value decreased. This can be attributed to the deprotonation

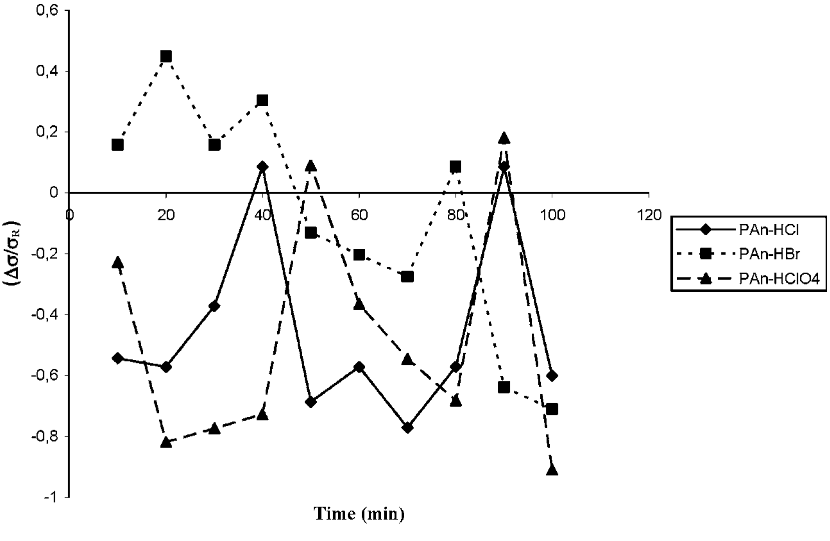


Figure 4. Changes of the electrical conductivity of PAns exposed to Et-OH.

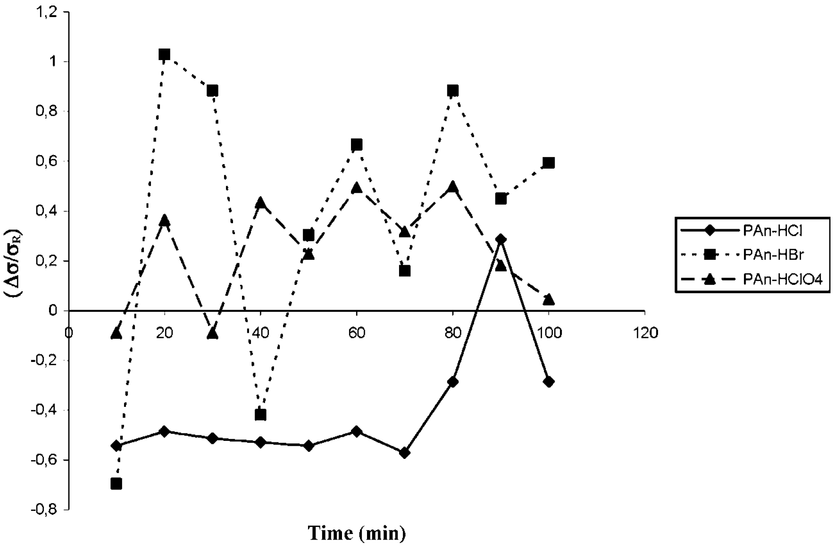


Figure 5. Changes of the electrical conductivity of PAns exposed to C_6H_6.

of PAn-ClO$_4$ salt causing a decrease in conductivity.[24] The sensing of PAn-HCl towards the HCl vapors is very low. The use of dopant material as an analyte may lead to doping, and excessive exposure may disturb the backbone of the doped polymer chain.

The conductivities of PAns were decreased by exposure to NH_3 vapors (Figure 2). The changes in conductivity of polymers are attributed to the consumption of charges from the polymeric backbone.[25] The sensing mechanism is explained by the compensation effect.[26] When the conductive emeraldine salt is exposed to NH_3 gas, the dopant is partially reduced, which leads to a decrease of electrical conductivity.[10] Extensive studies of the gas-sensing properties of conducting polymers show that when these polymers are exposed to electron-donating gases such as ammonia, if the gases are absorbed, the polymers exhibit an increase in resistance,[27] while an increase in conductivity is observed with gases such as HCl.[28,29] Polar solvents affect the conductivity of the materials via dipolar interaction with the radical cation and the protonated imine N center and by the subsequent deprotonation process. Koul et al.[24] have recently reported deprotonation as the basis for ammonia sensor activity of PAn composite. The less-polar solvents, instead of deprotonation, take part in disruption of π-electron delocalization and charge carrier transport through interaction between radical cations and their negative dipole ends.

The responses of PAns to chloroform vapor are presented in Figure 3. Chloroform exhibits weak acidic characteristics and is also known to act like a reducing gas. The decreased conductivity of PAns on first exposure to chloroform is indicative of interaction of chloroform molecules at dopant sites, i.e., N^+-H sites created by Cl^-. It may be highly probable that chloroform molecules attack the dopant site, causing neutralization of loosely bound couples formed with Cl^-, leading to a significant decrease of conductivity.[30] The solvent molecules or their pair with negative dipole on Cl act as electron suppliers to doped imine site and neutralize the positive charge.[29] This reduction nullifies the polaron charge carrier and leads to a fall in conductivity. But, on successive exposure, deviation from this order is observed.

All polymers respond to the saturated ethanol and benzene vapors by undergoing change in their conductivities (Figures 4 and 5). Negative changes in conductivities were observed upon exposing the PAn-Cl and PAn-ClO_4 to ethanol, whereas the opposite was observed for PAn-Br. The changes in conductivity of polymers can be attributed to the differences in their anions. Dopant anions have different size, and ethanol vapors can differently diffuse in the polymeric matrix.[31] The presence of the ethanol vapor could: (i) oxidize or reduce the polymer, changing the number of charge carriers on the polymer chains; (ii) interact with the mobile charge carriers on the polymer chain and affect their mobility; (iii) modify the potential barrier for the doping process of charge carriers between the polymer chains; or (iv) interact with dopant molecules.[32] It is considered that mechanism (i) is a likely process for PAn-HCl and PAn-$HClO_4$ chains. The increase in steady-state conductivity of PAn-HBr (i.e., that observed following the initial current transient) may be attributed to the dielectrical properties of the vapor molecules.[33]

CONCLUSIONS

In this article, we have presented HCl, NH_3, $CHCl_3$, EtOH, and C_6H_6 sensors based on PAn-Cl, PAn-Br, and PAn-ClO_4 polymers. Various anion-doped polyanilines can detected polar and weak polar molecules by their conductivity changes. The sensor properties of PAns varied depending on the nature of dopant anions. Low cost and easy fabrication can make this sensor suitable for use in chemical industries.

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