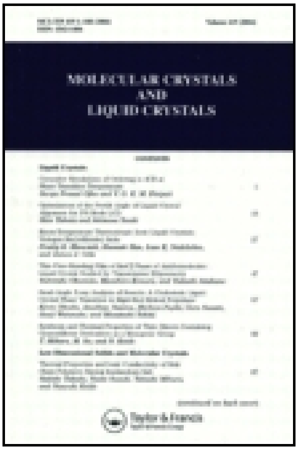

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Conductivity of Thin Polymer Films Containing Polyaniline

J. Haberko[1], J. Raczkowska[2], A. Bernasik[1], J. Rysz[2], M. Nocuń[3], J. Nizioł[1], W. Łużny[1], and A. Budkowski[2]
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Thin polymer films containing polyaniline doped with several organic dopants were manufactured and their conductivity was measured. The effect of chloroform vapour on the composite film conductivity was examined. The possibility of fabricating polyaniline-based chemiresistors working as gas detectors was taken into consideration. Resistivity of polymeric films patterned by Solvent Assisted Micromolding was also studied. Furthermore, impedance spectroscopy measurements were performed of thin films of pure doped polyaniline and of its blend with an insulating polymer.

Keywords: conductivity; gas sensors; patterning; polyaniline; thin films

1. INTRODUCTION

Intrinsically conducting polymers, such as polythiophene, polypyrrole or polyaniline, have been intensively utilised recently for the fabrication of various types of gas detectors. A comprehensive review can be found in [1]. In case of chemiresistors, interaction of a gas with a polymer film changes conductivity of the sensor via a chemical

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reaction or weak interaction (e.g. swelling or hydrogen bond formation) with the polymer. The authors of [2], for example, have shown that NO_2 partially oxidizes a polyaniline thin film thus raising its conductivity, whereas conductivity is diminished in the presence of N_2 gas as the result of removing residual water from the film. The authors of [3] demonstrated that a thin film of nanocrystalline Fe-Al-doped PANI is a good sensor of carbon monoxide. In this case CO physically absorbs on the polymer surface lowering the energy barrier between PANI crystallites and raising the overall conductivity of the material.

In field effect transistors and diodes using polymers as active semiconducting layers or electrodes, interaction with gases changes the source-drain current (FETs), turn-on voltage or rectification ratio (diodes). Active layers may be produced by a range of techniques, such as electrochemical deposition, spin-coating, Langmuir-Blodgett technique, thermal evaporation and others.

In the present study thin films containing polyaniline doped with various organic dopants were manufactured, including camphorsulfonic acid (CSA), dodecylbenzenesulfonic acid (DBSA) and diphenyl phosphate (DPHP). The films were obtained by spin-coating. Their conductivity was measured by means of the two-point and the four-point technique. Moreover, impedance spectroscopy measurements were performed. The influence of inert gas ($CHCl_3$) vapour on the conductivity of PANI (CSA)/PS chemiresistors was studied. Furthermore, conductivity of thin films patterned by means of Solvent Assisted Micromolding (SAMIM) was also investigated.

2. EXPERIMENTAL

The following procedure was applied to produce PANI(CSA) and PANI(DPHP) films:polyaniline EB (Aldrich, $M_W = 5\,k$ a.m.u.) and camphorsulfonic acid (Aldrich) or diphenyl phosphate (Aldrich) with a molar ratio of one dopant molecule per two polyaniline phenyl groups were dissolved in chloroform and mixed for 24 h. The solution was filtered through a Whatman Puradisc 0.2 μm teflon filter and in some cases polystyrene (PSS Mainz, $M_w = 125\,k$ a.m.u., $M_w/M_n = 1.04$) was added. Later on the solution was either spin-cast onto the substrate or spilled onto the substrate and left to dry. The latter allowed for the production of thicker films (several μm). Structural formulas of chemical compounds used in this study can be found in Figure 1. The procedure to obtain PANI(DBSA) films was slightly different: first polyaniline and DBSA (Aldrich, 70% wt. solution in isopropanol), with the same molar ratio of DBSA to PANI as above, were mixed in isopropanol for 24 h. Later on the solution was dried

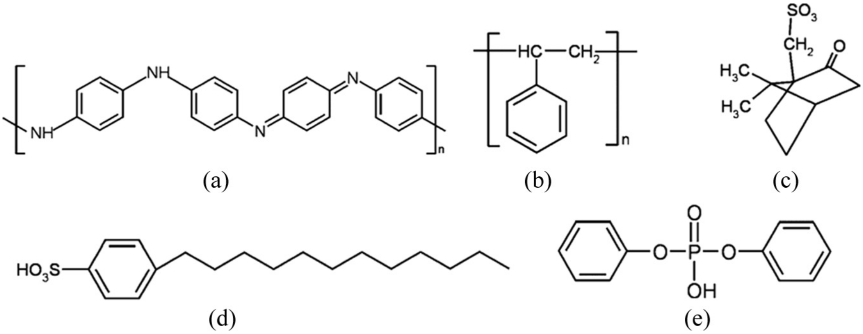


FIGURE 1 Structural formulas of compounds used in this study (a) polyaniline, (b) polystyrene, (c) camphorsulfonic acid, (d) dodecylbenzenesulfonic acid, (e) diphenyl phosphate.

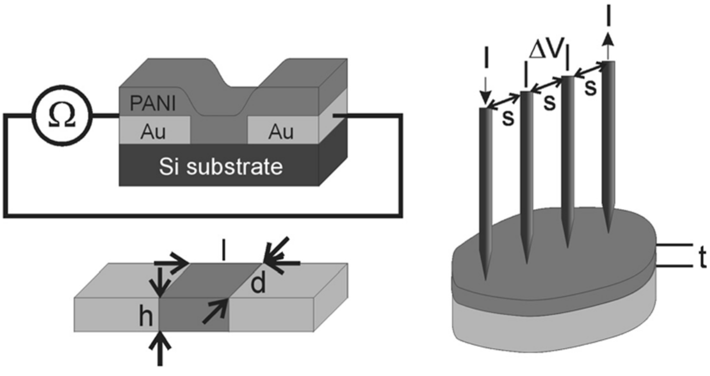
in a vacuum oven at 70°C for 24 h. The resulting dark green and slightly sticky, due to the presence of excess DBSA, powder was dissolved in chloroform and mixed for another period of 24 h. The solution prepared in this way was filtered and spin-cast onto the substrate.

A glass slide was used as substrate. The slide was cleaned and sonicated in toluene prior to use. Conductivity of the thin films was measured by means of the two-point and the four-point technique. In case of the former, two gold electrodes were evaporated on a glass substrate before spin-coating. A high work function metal (Au) was chosen in order not to allow for the formation of a Schottky barrier between the electrode and the polymer. In the four-point measurements a four-point probe with the distances between electrodes $s = 0.8\,\mathrm{mm}$ was pressed to a thin film on a glass substrate. The current-voltage characteristics were measured with a Keithley 487 picoammeter and a Keithley 2000 multimeter.

Furthermore, impedance spectroscopy measurements were performed on a pure CSA-doped polyaniline film and on a composite film containing PANI(CSA) and polystyrene. In this case a HIOKI 3532 device was utilised with a frequency range of 50 Hz to 5 MHz.

3. RESULTS AND DISCUSSION

In the two-point technique (see experimental setup in Fig. 2a) resistivity was established from a formula $\rho = R(hd/l)$, where h, d, l–dimensions of the conducting film (see Fig. 2a). The thickness of the films h was measured by means of atomic force microscope and



(a) (b)

FIGURE 2 Experimental setup for conductivity measurements a) two-point technique (b) four-point technique.

the distance between electrodes l upon observation under a metallographic optical microscope.

In the four-point technique resistivity of a conducting film can be established from a formula [4]: $\rho = 2\pi s f(\tau)\Delta V/I,\ \tau = t/s$, where $f(\tau)$ is a geometric correction factor and t, s are the film thickness and the distance between electrodes, respectively. For a given type of substrate (conductive or insulating) the $f(\tau)$ function can be approximated with any desired precision. In the limit case: $\lim_{\tau\to 0} \tau f(\tau) = 2\ln(2)$. In the present study $t \leq\ 5\,\mu\text{m}$, so $\tau \leq 6.25\cdot 10^{-3}$. Therefore, it can be assumed that $\tau f(\tau) = 2\ln(2)$ and $\rho = 4\pi \ln(2)(s^2/t)(\Delta V/I)$.

The results of conductivity measurements are presented in Figure 3. As can be seen from the graph, thin films with conductivity up to 7 S/cm were manufactured. Furthermore, it can be noticed that the film thickness influences its conductivity. This effect can be explained in terms of drying time, whose value is noticeably higher in case of thick films. There is more time for the formation of bigger and better-organised conducting PANI domains, which results in an enhanced probability of charge carrier hopping between macromolecules within domains and higher conductivity of the film.

Moreover, presence of polystyrene in the film considerably lowers its conductivity with respect to a pure doped PANI film. In this situation a conducting percolation network of PANI(CSA) domains in the matrix of polystyrene is formed. With the growing volume fraction of polystyrene the network tends to get more loose, hence its conductivity drops.

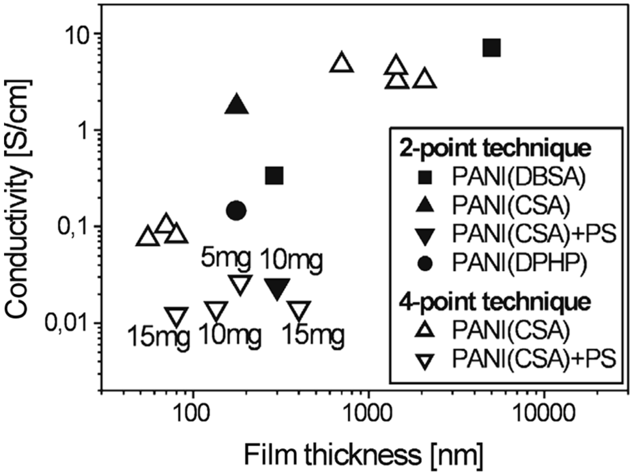


FIGURE 3 Results of conductivity measurements of thin films containing polyaniline with various dopants and of PANI(CSA)/PS composite films: □ PANI(DBSA), ▲ PANI(CSA), ▼ PANI(CSA)/PS composite, ● PANI(DPHP). Full symbols refer to 2-point measurements and open ones to 4-point measurements. Figures designate polystyrene content in the solution (5 mg/ml, 10 mg/ml or 15 mg/ml).

Conductivity of thin films containing a conjugated polymer may by altered by the presence of a gas, which allows for the fabrication of polymer-based gas sensors. In the present study a polymer blend containing PANI(CSA) and PS was spin-cast with a resistance of 667 MΩ (I-V graphs are presented in Fig. 4). Later on the film was dried in vacuum at 70°C for 20 min and its resistance was measured again, yielding a smaller value of 348 MΩ. This effect may be attributed to evaporation of residual solvent from the film and possibly additional doping of polyaniline by free CSA molecules in high temperature. In the next step the film was placed in a glass chamber with copious amounts of $CHCl_3$ vapour and kept in room temperature for another 20 minutes. After this procedure the resistance of the sample rose to 476 MΩ. This result can be explained as the effect of swelling of the insulating matrix. Chloroform is a better solvent for polystyrene than for doped polyaniline, hence in the presence of its vapour conducting PANI domains swell only slightly, whereas the volume of PS matrix can grow considerably. As a result the average distance between PANI domains grows and the probability of charge carrier tunneling drops, resulting in the diminished conductivity. A model of the sample microstructure before and after exposition to chloroform

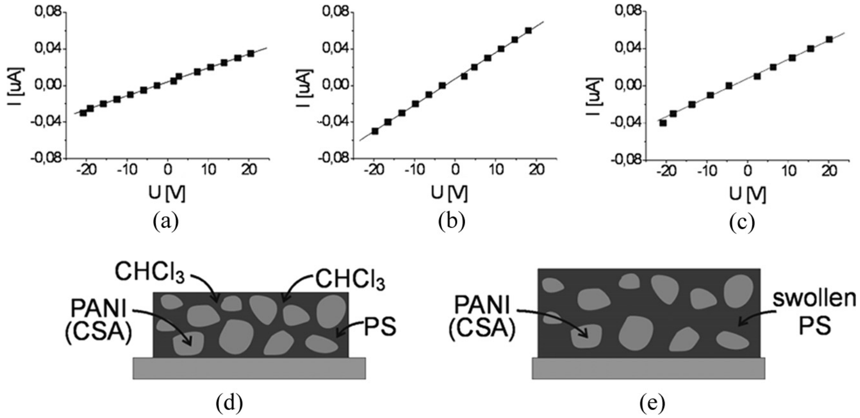


FIGURE 4 Influence of chloroform vapour on the conductivity of PANI(CSA)/PS composite film. I-V graphs of the film (a) immediately after spin-coating, (b) after drying at 70°C for 20 minutes, (c) after subsequent exposure to chloroform vapour for 20 minutes. A model of PANI(CSA)/PS film microstructure (d) before and (e) after exposition to chloroform vapour.

can be found in Figures 4(d and e). All measured I-V characteristics are linear and ohmic contacts between the polymer and the electrodes are formed.

Furthermore, conductivity of films patterned via Solvent Assisted Micromolding (SAMIM) was studied. In this technique a uniform polymer film (here, PANI(CSA)) is spin-cast on a glass slide with evaporated electrodes. Later on, a PDMS stamp with a pattern of protruding stripes (here, the thickness of a stripe is 6 μm and periodicity of the pattern 20 μm) is wetted with a solvent ($CHCl_3$), pressed against the substrate and left under load to dry (Fig. 5). The direction of the stripes is perpendicular to a gap between the electrodes. The resistance of the film immediately after spin-coating was equal to 9.8 MΩ. After patterning the resistance increased to 18.8 MΩ. This was caused by the fact that the overall cross-section of the patterned film is smaller than that of the uniform one. However, when the patterned film was rinsed with chloroform it appeared that it was impossible to remove all the polymeric material from the substrate, as can be seen in an optical micrograph in Figure 5c. Moreover, the resistance of the film decreased to 1.8 MΩ. This unexpected result may be explained as follows: pressing the polymer film to the substrate with a PDMS stamp enhances the specific interaction of polyaniline with gold. As a result it is no longer possible to remove the polymer by simply rinsing the sample with a solvent. During rinsing the domains that

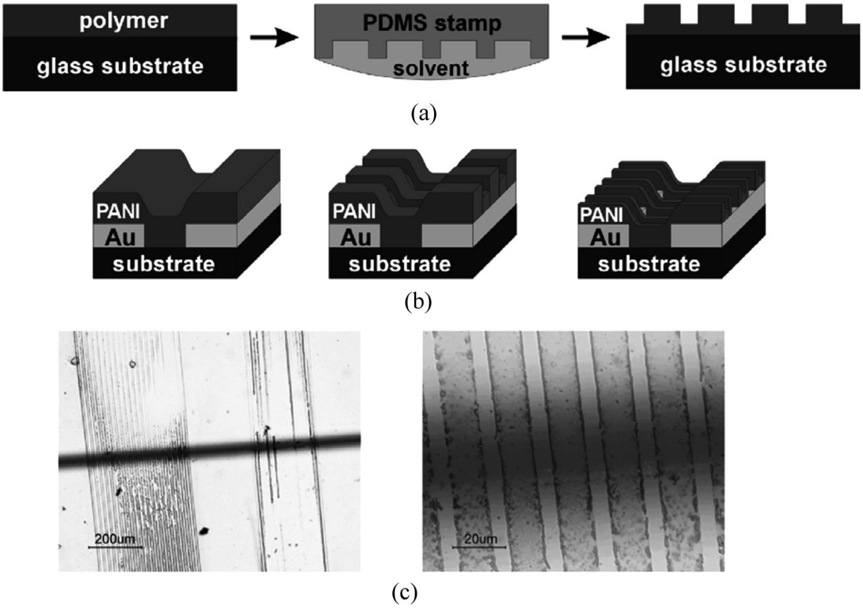


FIGURE 5 (a) Patterning a polymer film via Solvent Assisted Micromolding (SAMIM), (b) a model of the thin film after spin-coating, after patterning and after rinsing with $CHCl_3$, (c) optical micrographs of the film after rinsing with $CHCl_3$.

are weakly bound to the substrate are removed, and the strongly-bound ones grow and their organisation is improved resulting in an increased conductivity.

Impedance spectroscopy measurements of the investigated thin films showed significant differences between a pure PANI(CSA) film and a thin film composite. In the former case (PANI(CSA) film, thickness 1.1 μm, obtained by casting from a solution) only one semicircle on a Im(Z) vs. Re(Z) plot can be observed (Fig. 6a). The polymeric material in this case can be substituted with a simple electrical circuit consisting of a resistor and a capacitor connected in parallel, a circuit with only one time constant. Only one type of conducting domains can be seen within the accessible experimental range. A similar plot for a 4.8 μm PANI(CSA)/PS film, cast from a solution containing 6 mg/ml PANI(CSA) and 10 mg/ml PS, contains two impedance semicircles (Fig. 6b) and a circuit with two time constants is needed to explain the material's electrical behaviour. One can distinguish between two types of conducting domains, one rich in PANI(CSA) and another rich

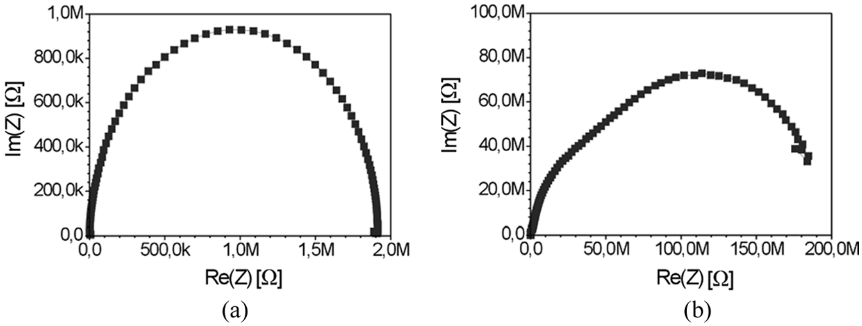


FIGURE 6 Impedance spectra of thin films: (a) pure PANI(CSA), thickness 1.1 μm, (b) PANI(CSA)/PS composite, thickness 4.8 μm.

in PS. This result attests to the fact that both phases appearing after the spinodal decomposition, which takes place during the film drying, contain both the conjugated and the conventional polymer; however, in different ratios.

CONCLUSIONS

In conclusion, in the present study thin films containing doped polyaniline with relatively high conductivity were manufactured. Their conductivity was measured by means of the two-point and the four-point technique. Moreover, it was shown that the conductivity of composite PANI(CSA)/PS films decreases in the presence of chloroform vapour as a result of the non-conducting phase swelling. Conductivity of films patterned by the SAMIM method was also investigated. It was shown that the resistivity of a patterned film decreases as a result of treatment in chloroform, probably due to rearrangement of highly conductive well-arranged domains. Finally, impedance spectroscopy spectra show two types of conducting regions in the sample in case of a PANI(CSA)/PS composite, whereas only one type of domains can be seen in pure polyaniline films.

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