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Electrical and Physico-Chemical Properties of Nanolayers of Conducting Polyaniline-Polystyrene or Camphor Sulfonic Acid Blends

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Summary: In this work we studied the physico-chemical and electrical properties of conducting blends of polyaniline (PANI) with polystyrene (PS) or camphor sulfonic acid (CSA) in an appropriate solvent such as m-cresol using various concentrations of PS. The thin films or nanolayers prepared by spin coating were analysed by ellipsometry (to measure the thickness), dynamic contact angle (to measure the surface energy), atomic force micropsopy techniques (to observe the topography and roughness of films), and by using a Keithley SMU 236 recorder under a vacuum of 10^{-3} mbar, to determine the variation of the current as a function of the voltage. Results obtained show that the variations of current I versus of the voltage V (from –15 V to +15 V) for all samples coated on silicon substrate indicate a barrier effect that becomes more and more important with the increase of the PS content, while samples prepared on a glass substrate give a linear variation of the current according to the voltage. These observations (load space limited current, Fowler-Nordheim tunneling effect, light-emitting diodes) will be described in this paper.

The electrical conductivity of the PANI-CSA-PS blends at room temperature for different concentrations of polystyrene (from 0% to 50%) was measured by the four probe method as a function of the PANI weight fraction x. It seems that when x increases the electrical conductivity σ increases and reaches a threshold for $x = 0.5$ and $\sigma = 8.5$ S/cm.

Introduction

The interest in conducting polymers extremely increases since about twenty years. These polymers present some very interesting electronic properties by chemical or electrochemical oxidation and they are very important in several industrial domains (electrochemistry, rechargeable cells, the electronic devices, lithography, etc).[1-3] This interest resides in the different methods of synthesis that permit a good control of their electronic properties. Besides, these materials present the advantage to be lighter than metals and less expensive.[4]

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We were interested in this work to study the physico-chemical and electrical properties of conducting blends of polyaniline (PANI) and polystyrene (PS) or camphor sulfonic acid (CSA) in an appropriate solvent as m-cresol using various concentrations of PS.

Principle of the polyaniline doping

Formulas of polyaniline

Under the name of polyaniline, we group a family of polymers having different degrees of oxidation. The various forms of polyaniline (PANI) are given by the general formula in Figure 1.

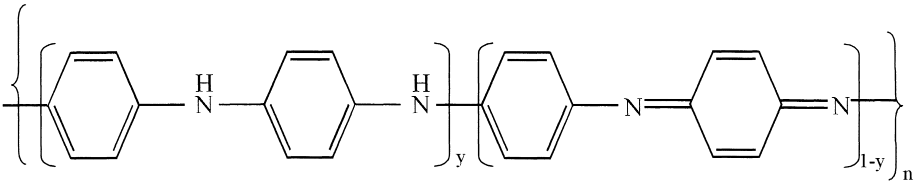

Figure 1. Principal forms of polyaniline.

(1-y) represents the mean degree of oxidation that will be limited between 0 and 1. Mc Diarmid et al.[5] proved that the three unique oxidation numbers are 0, 0.5 and 1. By protonation in acid medium, polyaniline will give three types of salt according to the oxidation states: polyleucoemeraldine (1-y = 0), polyemeraldine (1-y = 0.5) and polypernigraniline (1-y = 1).

Doping of polyaniline

Conducting polymers have the particularity to become conductor by the action of an oxidant or a reductor. In fact, these polymers are doped. We distinguish between two principle ways of doping of polyaniline:

Doping by oxidation

In presence of an oxidant, we obtain the polyemeraldine salt according to the following reaction given in Figure 2.

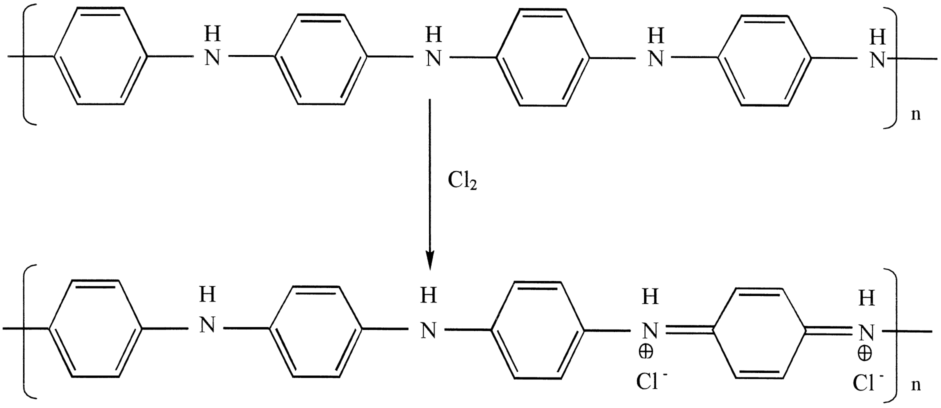

Figure 2. Oxidation of polyleucoemeraldine.

Doping by protonation

In presence of an acid, e.g. HCl, the polyemeraldine base gives by protonation the polyemeraldine salt (cf. Figure 3).

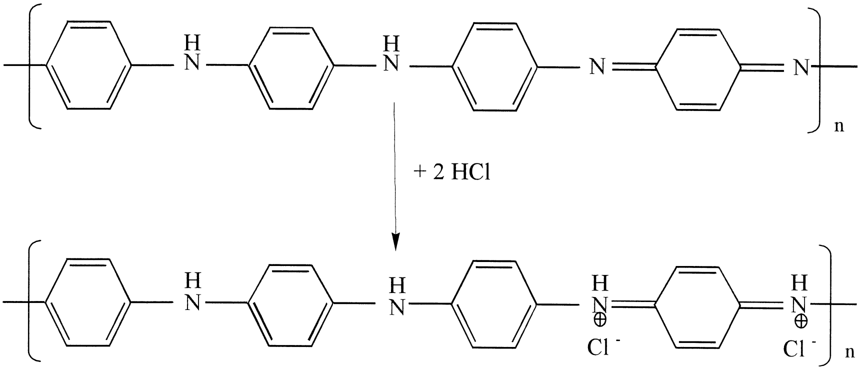

Figure 3. Protonation of polyemeraldine base.

Other doping ways can be realised: the secondary doping.

Secondary doping

In that case, the solvent plays the role of the secondary dopent for the polyaniline doped with a functionalised sulfonic acids, such as camphor sulfonic acid (CSA). The formula of CSA is given in Figure 4.

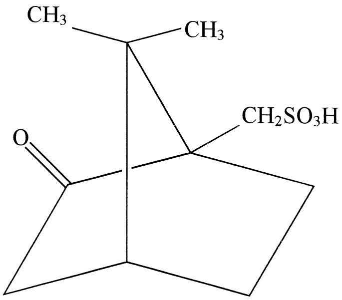

Figure 4. Formula of the camphor sulfonic acid (CSA).

Blend with polystyrene (PS)

The basic characteristics of PS are its transparency, its lightness and its good mechanical properties. The films obtained by using PS present an excellent mechanical durability.

PANI can be dissolved in several common solvents such as m-cresol, toluene, and chloroform. In our case, to obtain PANI-PS blends, a PS solution was prepared by dissolving PS in m-cresol.

Experimental results

Wettability

Principle and experimental determination of the surface energy of a solid [6,7]

The method used here is the classical method of Young and Young-Dupré [8,9] (cf. Figure 5).

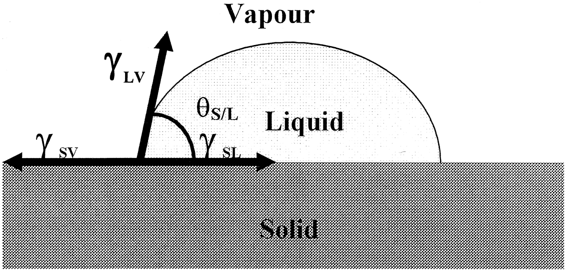

Figure 5. Young model.

Where γ_{SV} is the surface free energy of solid in presence of vapour, γ the surface free energy of solid in presence of liquid, γ_{LV} the surface free energy of liquid in presence of vapour, and $\theta_{SL/V}$ the contact angle of liquid on solid.

Equilibrium condition will be written:

$$\gamma_{SV} = \gamma_{SL} + \gamma_L \cos\theta_{SL/V} \tag{1}$$

Taking into account the two-dimensional pressure:

$$\gamma_{SV} = \gamma_{SL} + \gamma_L \cos\theta_{SL/V} + \Pi_e \tag{2}$$

Adhesion energy W_{SL} will be given by Young - Dupré equation:

$$W_{SL} = \gamma_L (1 + \cos\theta_{SL/V}) + \Pi_e \tag{3}$$

Using interaction energies due respectively to the dispersion forces I_{SL}^d and to the polar interaction forces I_{SL}^P, we obtain:

$$\cos\theta_{SL/V} = \frac{2\sqrt{\gamma_S^d \gamma_L^d}}{\gamma_L} + \frac{I_{SL}^P}{\gamma_L} - 1 \tag{4}$$

Plotting $\cos\theta$ as a function of $\sqrt{\gamma_L^d}/\gamma_L$ as shown in Figure 6 for polar and non-polar liquids, we obtain the following straight line. The slope of this straight line allows to obtain the dispersive component of surface energy of the solid; whereas, the distance between the two ordinates of the representative point of a polar liquid and the point belonging to the experimental line and having the same abscissa will give the specific interaction between the polar molecules and the solid substrates.

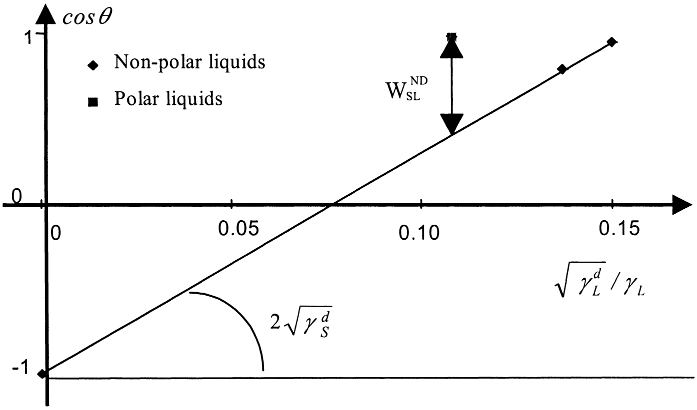

Figure 6. Experimental determination of the surface energy components of a solid.

Experimental results

The measurements were carried out using the tricresylphosphate (TCP) and the Diiodomethane as non-polar liquids and water as polar liquid. Table 1 gives the measurements done with polyaniline 0.5 g/L, by varying the CSA concentration. The substrate is the silicon wafer.

Table 1. Evolution of the surface energy γ and contact angle θ as a function of the concentration of CSA.

concentration of dopent CSA (g/L)	0	0.1	0.2	0.3	0.4	0.5
θ_{TCP} (°)	08 ± 1	39 ± 2	37 ± 4	29 ± 1	30 ± 3	23 ± 3
$\theta_{Diiodomethane}$ (°)	42 ± 1	53 ± 1	54 ± 1	54 ± 3	50 ± 1	54 ± 2
γ_S^d (mJ/m^2)	42 ± 2	34 ± 1	34 ± 3	36 ± 5	37 ± 3	37 ± 7

Other measurements were done by varying the concentration of polystyrene, we obtain Table 2.

Table 2. Evolution of the surface energy γ and contact angle θ as a function of the concentration of PS.

concentration of dopent PS (g/L)	0	0.1	0.2	0.3	0.4	0.5
θ_{TCP} (°)	0	0	0	0	0	0
$\theta_{Diiodomethane}$ (°)	19 ± 1	49 ± 8	51 ± 8	55 ± 5	64 ± 3	54 ± 2
γ_S^d (mJ/m^2)	50 ± 1	36 ± 8	36 ± 8	33 ± 6	28 ± 3	33 ± 4

By using the glass substrate, we obtain the results given in Table 3.

Table 3. Evolution of the surface energy γ and contact angle θ as a function of the concentration of PS with the glass substrate.

concentration of dopent PS (g/L)	0	0.1	0.2	0.3	0.4	0.5
θ_{TCP} (°)	/	47 ± 3	45 ± 5	49 ± 8	54 ± 6	46 ± 6
$\theta_{Diiodomethane}$ (°)	19 ± 1	60 ± 3	57 ± 6	56 ± 6	55 ± 3	47 ± 1
θ_{water} (°)	0	43 ± 8	43 ± 5	44 ± 4	45 ± 3	53 ± 4
γ_S^d (mJ/m^2)	50 ± 1	30 ± 3	31 ± 3	30 ± 4	29 ± 1	33 ± 3
W_{SL}^{ND} (mJ/m^2)	78 ± 1	74 ± 2	73 ± 2	73 ± 3	72 ± 1	62 ± 2

Partial conclusion

- The surface energy of the films of conducting polyaniline is not affected by the nature of the dopent.
- However, a decrease of the polyaniline concentration changes the polarity of the analysed surfaces.

Ellipsometry

PANI-CSA-PS films were prepared for various weight percentages of PS. The thickness of the films obtained was determined by the ellipsometry technique. The results obtained allowed to plot the curve given in Figure 7.

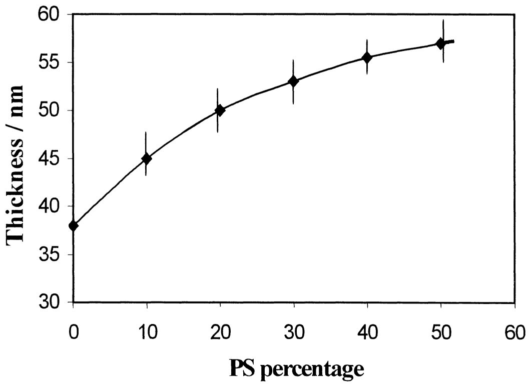

Figure 7. Evolution of the film thickness as a function of the content of PS.

Figure 7 shows that the thickness increase when the percentage of PS increase but the increase is slower when the polystyrene concentration is more than 30%. Results obtained by ellipsometry technique were used to determine the electrical properties of the different films.

Electrical properties

Two groups of polyaniline doped by the camphor sulfonic acid with polystyrene (PANI-CSA-PS) for various concentrations, were prepared and studied :

1- The first samples were deposited on glass substrates. We measured the electrical conductivity of such samples.

2- The second samples were deposited on silicon substrates. We determined the characteristics current-voltage of such samples.

Electrical conductivity

The electrical conductivity of the different films was measured by using the Van der Paw method. The electrical contacts were realised in four points of the sample by the help of a silver lacquer. The method used is called the four-probe method.[10-15]

We measured, by this method, the electrical conductivity of PANI-CSA-PS blends at room temperature by varying the percentage in weight of PS between 0 and 70%. The results obtained are showed in Figure 8 which gives the electrical conductivity σ of the films as a function the weight ratio of PS.

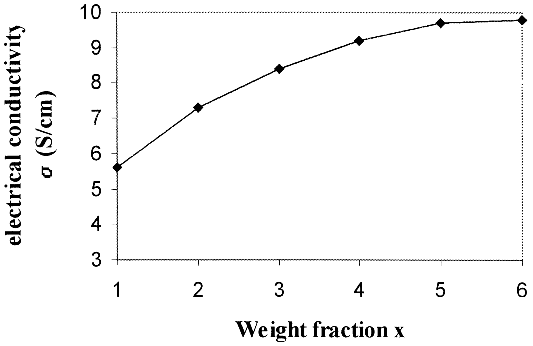

Figure 8. Variation of the electrical conductivity as a function of the weight fraction of PS.

The value of σ obtained with PANI-CSA for $x = 0.5$ is equal to $\sigma = 9.5$ *S/cm* which is in good agreement with that obtained in the "Institut des Matériaux de Nantes" with identical but thicker samples (the thickness is about some micro-metres).[16,17]

Current-voltage characteristics

The samples of the second group of PANI-CSA-PS were deposited on silicon substrates. The electrical contacts were realised by using two electrodes as shown in Figure 9 and the lacquer silver.

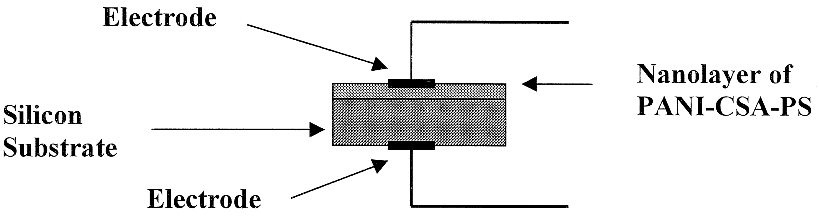

Figure 9. Experimental principle.

The current-voltage characteristics of the different samples were measured by means of a Keithly SMU (Model 90 / Metrics *I-u*) under a vacuum of 10^{-3} mbar.

The results obtained show that the variations of current *I* versus of the voltage *u* (from −15 V to +15 V) for all samples coated on silicon substrate indicate a barrier effect that becomes more and more important with the increase of the polystyrene percentage (Figure 10), while samples prepared on a glass substrate give a linear variation of the current according to the voltage.

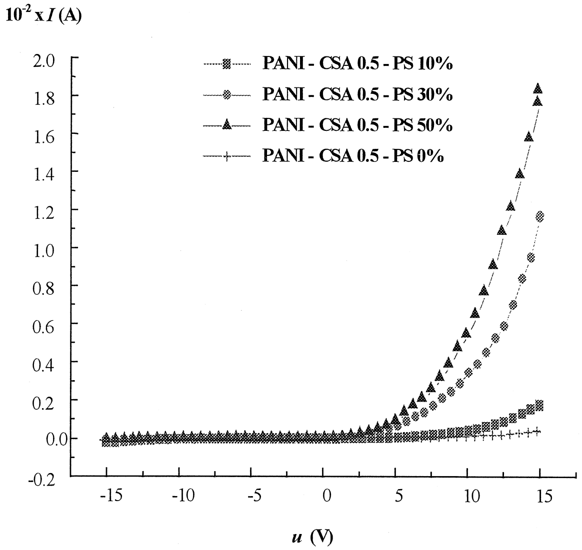

Figure 10. Variation of the current I as a function of the voltage *u* of different samples.

Analysis of the (*I-u*) data and conclusions

We tried to model the various experimental curves (*I-u*) (Figure 10) obtained by a law given by equation 5 :

$$I = I_0 \left[exp\left(\frac{qu}{nkT} \right) - 1 \right] \tag{5}$$

Where q is the electronic charge, $n \approx 1$ the ideality factor, k the Boltzmann constant, I_0 the saturation current and T the absolute temperature.

However, this law given by equation 5 is not valid for all samples of polyaniline doped with CSA for various concentrations of PS and cannot fit the data well, suggesting that the current is not controlled by thermionic emission over an energy barrier at the organic heterointerface or at the contacts.

We then tried to apply another law (Fowler-Nordheim tunneling effect) of the type:

$$I \propto exp\left(\frac{-1}{u} \right) \tag{6}$$

Even this law cannot describe well all curves (*I-u*) obtained with the various films. The application of the Fowler-Nordheim expression [18] to our results is also poor in the high field region, suggesting that tunneling from contacts or between bands is not a significant limiting factor in current conduction

In fact, the variation of the current as a function of the voltage follows the law given by equation 7 for $m \geq 2$:

$$I \propto u^{m+1} \tag{7}$$

This law ($m \geq 2$) is in good agreement with our experimental results. This leads to the conclusion that the electronic conduction is done with the help of the space charge limited current (SCLC) effect. The same results were observed by Burrows and Forrest in 1994 [19] and Blom et al. in 1996 [20] on different materials. The power-law dependence of the *I-u* characteristics over m orders ($m \geq 2$) of magnitude in current strongly suggests that the electron current in doped PANI is primarily dominated by space-charge injection effects.

The current-voltage characteristics obtained with the different samples will allow to conclude that the PANI nanolayers doped by CSA will be good candidates to be used as components in the elecroluminescent diodes.

Extension of this study

To confirm the aptitude of such materials to be used as elecroluminescent polymers for the fabrication of light-emitting diodes (LEDs), we propose to continue this study by varying the different physico-chemical parameters of the doped films, as the film thickness, the temperature, the dopent nature, the various concentrations, and the solid substrates and then to optimise the different properties.

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