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High Pressure Conductivity and Photoconductivity of Polyveratrole

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Summary

Electropolymerization of o-$(CH_3O)_2C_6H_4$ (Veratrole) in dry acetonitrile / tetrabutyl-ammonium tetrafluoroborate at platinum electrode, yields a green polymeric conducting solid. As the pressure is increased, the material becomes more conductive, but sharp changes towards lower conductivity occur at 4.2 and 6.2 metric tons pressure, probably due to phase transitions. The photoconductivity shows an exponential increase as temperature is increased, but it shows reversible changes at 200 K, 225 K and 250 K during slow warming, also attributable to phase transitions. Photoconductivity of Polyveratrole increases with the radiation frequency, being higher under blue light than under red of infrared radiation and there is a linear increase of photoconductivity with radiation density. Conductivity transients show that the conductivity increases exponentially with time to the saturation point within few minutes, and it also decreases exponentially when the light is turned off and the circuit is open. This behaviour can be explained by formation and encounter of electron and hole as current carriers. A preliminary study indicates a piezoelectric effect for the material. absorption spectroscopy allowed the measurements of the material band gap.

Introduction

Organic compounds have the potential to serve as molecular components of electronic devices. It is possible to introduce negative or positive charge to electrically conjugated organic molecules by electrochemical oxidation or reduction. Veratrole (1, 2-dimethoxybenzene), can be electrochemically oxidized in acetonitrile / tetra-butylammonium tetrafluoroborate (using a Pt electrode), at room temperature, leading to a supramolecular species, insoluble in most of common solvents (it is only soluble in trifluoroacetic acid) that has been named Polyveratrole according to scheme I (1,2). The electrochemical oxidation product of Veratrole is a dark green conducting solid that shows interesting properties [1, 2]. When an electron moves in a ionic crystal,

there is a polarization that creates some distortion of the structure and this has been defined as polaron [3]. In the case of organic conducting polymers, such species are better known as radical ions and the unpaired electron can be delocalized through the aromatic structure.

These materials develop a redox capacitance that enables them to store energy, making them good candidates as materials for batteries. A cell arrangement with Polyveratrole in its oxidized and reduced states, deposited on a platinum foil, could be used to run a small calculator [4]. Organic photoconductors as, for instance, *poly* (*N*-vinylcarbazole) belongs to the few examples where organic materials have penetrated sophisticated technologies like, xerography, laser-printing techniques, etc. In general, the low mobilities of organic photoconductors are due to trap dominated hopping transport between the pendants, photoconductive groups, giving rise to a certain localization of charge carriers [5 - 8]. In this paper, we will discuss interesting properties of Polyveratrole and we will give a theoretical model for the conductivity and photoconductivity of the material and the effect of changing the pressure and temperatures.
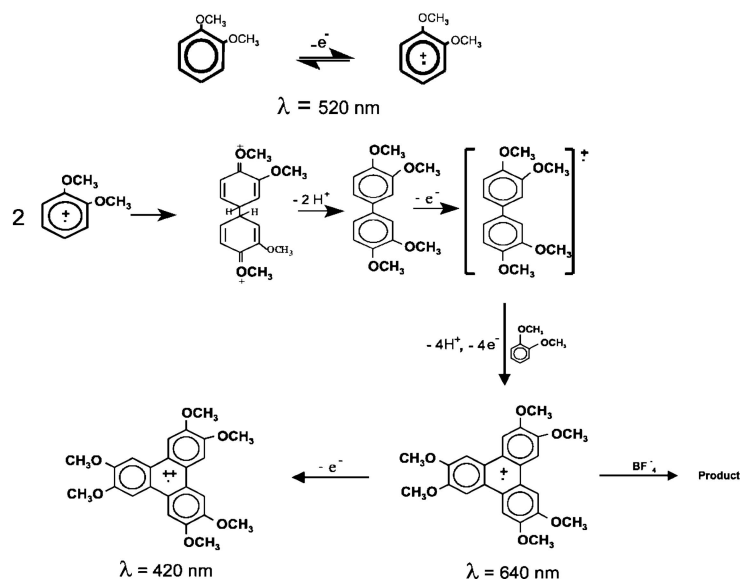
Scheme 1. Proposed sequence for formation of polyveratrole

Experimental

The solid is prepared according to procedures reported in previous works [1,2] and it is used directly without further treatment. The photoconductivity as a function of pressure and as a function of temperature is studied in this work. The photoconductivity high-pressure studies were carried out in a stainless steel cell specially designed for this work. The stainless steel (5mm thick) cell body has an internal diameter of 2.5 cm, a circular mica electrical insulating sheet is placed at the bottom of the cell, which is a Teflon cylinder equipped with a 1 cm cylindrical hole to contain the sample. Pressure is applied with a stainless steel piston. The cell is closed

with a stainless steel lid. The gold electrical wires pass through the lid, through the Teflon cylinder, contacting the sample from the bottom (Figure 1). A Carver high-pressure press (11 metric ton, 24000 pounds / inch^2 range) is used, and the resistance is measured with an HP instrument. Variation of resistance versus applied pressure is shown in Figure 2. The optical absorption spectra of the material was measured within the wavelength range between 550 and 850 nm at 300 K, using a modified Cary 17D spectrophotometer.
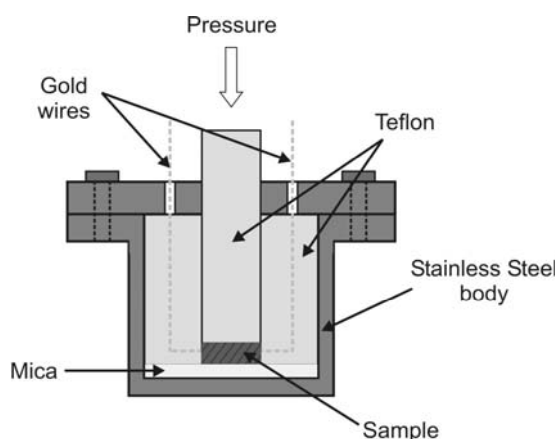

Figure 1. High Pressure Cell

The photoconductivity pursuit, as a function of temperature was done on a pressed sample (5 mm diameter, 1 mm thick, 3 metric tons pressure) with gold wires fixed with Ag paint, placed over a Cu support (plastic insulated and retained with silicon grease). The Cu support is placed in a cryostat equipped with quartz windows. Temperatures from 293 K to 79 K (Air Products Digital Temperature Indicator with thermocouple sensitive to ± 0.1 K) are obtained with a closed circuit He APD Cryogenics HC-2 system, under high vacuum (20 μm Hg, mechanical pump and oil diffusion pump). The sample was irradiated with monochromatic light focused from the exit slit of a Monospek 1000 simple monochromator with interchangeable gratings (visible: range 250 nm to 800 nm, and infrared: range 800 nm to 2000 nm, 100 Å / min scan) and a white light source (current stabilized W lamp). Due to the slow response of the material, it was not possible to use the frequency modulated light source even at the slowest frequency (60 Hz). The sample was also irradiated with white light (small flashlight) and with a laser (Ion Laser Technology, 5425 model, K$^+$ ion, 448 nm, and variable power to 10 mW, focused on the sample centre). The experiments performed at room temperature, were carried out in air, Ar or N$_2$ under atmospheric pressure or under vacuum. The conductivity and photoconductivity measurements were done applying a 2.0 V to the sample through the gold wire, measuring the current with an electrometer (Heathkit, nanoampere range) and plotting the response (Linear Instruments Corp., 261 Model recorder, and 1 mV sensitivity) versus time. The measurements were done in a dark room to minimize stray light falling on the sample. A preliminary study of the conductivity response with sound frequency was carried out by applying 2 V to the sample and the sound from a small tweeter focused on the sample with a glass funnel within the range 10 Hz to 100 kHz (Kenwood CR Oscillator AG-203), with and without laser irradiation.

Results and Discussion

High pressure studies

The microcrystalline solid obtained directly from the electrochemical synthesis is an air stable dark green powder that needs to be compacted to show some conductivity. As the pressure is increased (Figure 2) above 0.5 metric tons, resistance decreases (or conductivity increases) rapidly until a minimum resistance is observed near 2.2 metric tons.
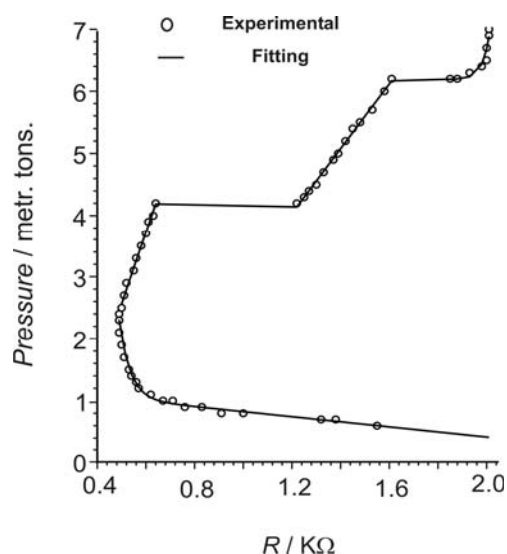

Figure 2. Effect of the pressure on the resistance of the sample

The change of pressure, as a function of the resistance, ranging the pressure up to 2.2 metric tons was fitted with equation (1):

$$P = p_3 + p_4\,R + p_1 \exp\left(-\frac{R}{p_2}\right) \qquad (1)$$

Where $p_1 = 69623.56$, $p_2 = 0.04492$, $p_3 = 1.2235$, $p_4 = -0.40775$ are the fitting values and R is the resistance in $K\Omega$.

At pressure values above 2.2 metric tons, a slight resistance linear increase is observed until the pressure reaches 4.2 metric tons. This change of resistance with the pressure obeys equation (2):

$$P = -3.2490 + 11.6219\,R \qquad (2)$$

A sharp increase in R is then observed at 4.2 metric tons (from 0.6 to 1.3 x 2 $K\Omega$), and a gradual linear resistance increase occurs up to 6.2 metric tons. This variation is given by equation (3):

$$P = -2.1878 + 5.18908\,R \qquad (3)$$

After 6.2 metric tons another sharp increase in resistance is observed, followed by a gradual resistance increase from 6.2 metric tons to 7.0 metric tons (the highest

pressure studied). Actually, the pressure varies exponentially with the resistance following equation (4):

$$P = 0.0048 \exp(0.0285\,R) \tag{4}$$

After relieving the applied pressure and returning to atmospheric pressure, the resistance remains very close to the highest value attained. The sharp conductivity changes at 4.2 and 6.2 metric tons suggest a phase transition of the material to a less conducting phase. The last phase recovered from the cell is a dark glassy material, showing an infrared spectrum, almost identical to that obtained with the green starting material, suggesting that the hexamethoxi- triphenylene ring still remains [1].

Temperature dependence of photoconductivity

Conductivity of Polyveratrole was studied as a function of temperature by changing the sample temperature from 80 K to room temperature in two different ways: firstly, by heating up (Figure 3) and then cooling down (Figure 4). The conductivity of the material decreases when it is cooled (from 293 K to 80 K, 4 degrees / min until 150 K and then programming the temperature at a rate of 2 degrees / min up to 80 K). As the temperature is slowly increased (by turning off the He cooler and letting it warm up slowly under vacuum, 2.5 degrees / min initially until 240 K and then 0.4 degrees / min until 280 K) there is an exponential increment of conductivity up to 200 K. After this point, the photoconductivity shows a different behaviour due to a phase transition (Figure 3). There are more pronounced conductivity increases at 225 K and 250 K, where there is a rapid rise until saturation and then, a gradual increase due to the temperature. The changes observed at those temperatures are reversible and suggest possible structural changes to more conducting phases.

When the sample is laser irradiated (λ = 448 nm) at 293 K under atmospheric pressure, there is an exponential current increase (Figure 5) to complete saturation. When the laser is turned off, the current decreases exponentially (Figure 6) to the
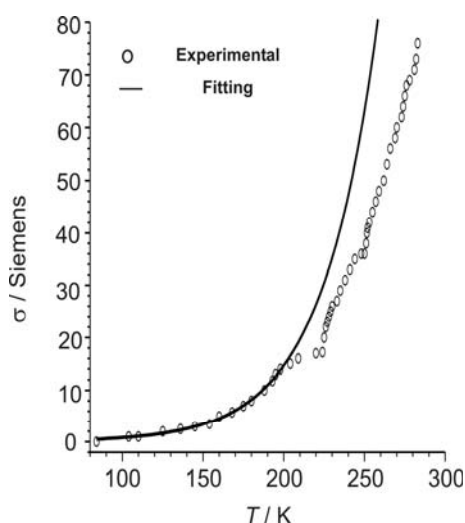

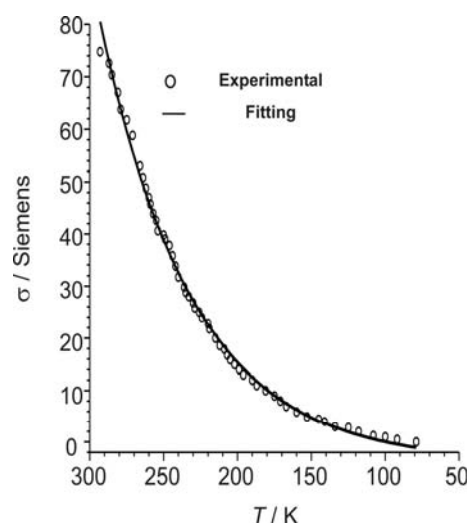**Figure 3.** Effect of temperature on the conductivity of the sample (heating)

Figure 4. Effect of temperature on the conductivity of the sample (cooling)

original level. This process is completely reversible and occurs without apparent sample damage or decomposition. The change of the photoconductivity $\Delta\sigma$ can be calculated using equation (5):

$$\Delta\sigma = e\left(\mu_n\,\Delta n + \mu_p\,\Delta p\right) \tag{5}$$

Where μ_n and μ_p are the electron and hole mobilities. Δn and Δp are the change of the density of states of electrons and holes, respectively, and e is the charge of the electron.

When the sample is illuminated, the conductivity rises to reach a maximum after some time. The variation of charges due to photogeneration, (n and Δp, with time can be calculated by:

$$\frac{d(\Delta n)}{dt} = \beta\alpha\phi - \frac{\Delta n}{\tau_1} \tag{6}$$

$$\frac{d(\Delta p)}{dt} = \beta\alpha\phi - \frac{\Delta p}{\tau_2} \tag{7}$$

Where β is the quantum efficiency (Charges generated by the incident photon), α is the absorption coefficient, ϕ is the absorbed energy in the semiconductor for area unit and time unit.

The initial condition for the ordinary differential equations are $\Delta n = 0$ and $\Delta p = 0$ when $t = 0$. The solution of these equations is:

$$\Delta n = \tau_1\beta\alpha\phi\left(1-\exp\frac{t}{\tau_1}\right) \tag{8}$$

$$\Delta p = \tau_2\beta\alpha\phi\left(1-\exp\frac{t}{\tau_2}\right) \tag{9}$$

Replacing of equations (8) and (9) into equation (5) yields equation (10):

$$\Delta\sigma = e\mu_n\,\beta\alpha\phi\tau_1\left(1-\exp-\frac{t}{\tau_1}\right) + e\mu_h\,\beta\alpha\phi\tau_2\left(1-\exp-\frac{t}{\tau_2}\right) \tag{10}$$

$$\sigma = \sigma_0 + e\mu_n\,\beta\alpha\phi\tau_1\left(1-\exp-\frac{t}{\tau_1}\right) + e\mu_h\,\beta\alpha\phi\tau_2\left(1-\exp-\frac{t}{\tau_2}\right) \tag{11}$$

When the incident light is switched off, the photoconductivity decays as a function of time. For this case, the rate of recombination of carriers is proportional to the density of carriers Δn and Δp.

$$\frac{d(\Delta n)}{dt} = \frac{\Delta n}{\tau_3} \tag{12}$$

$$\frac{d(\Delta p)}{dt} = \frac{\Delta p}{\tau_4} \tag{13}$$

Assuming that $\Delta n = \Delta n_s = e\mu_n\beta\alpha\phi\tau_1$ and $\Delta p = \Delta p_s = e\mu_h\beta\alpha\phi\tau_2$ for the initial conditions, the solutions of these differential equations are given by equations (14) and (15):

$$\Delta n = \Delta n_s \exp-\frac{t}{\tau_3} \tag{14}$$

$$\Delta p = \Delta p_s \exp-\frac{t}{\tau_4} \tag{15}$$

Replacing in equations (14) and (15) the values of Δn and Δp derived from equation (5), we can write down:

$$\sigma = \sigma_0 + e\mu_n\Delta n_s \exp-\frac{t}{\tau_3} + e\mu_h\Delta p_s \exp\frac{t}{\tau_4} \tag{16}$$

The experimental results for the photoconductivity of the sample when the incident light of the laser is on are shown in figure 5.
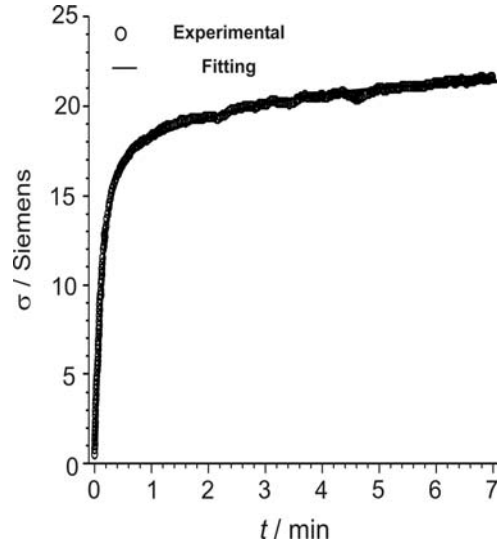

Figure 5. Conductivity transient while illuminating the sample with the laser at 293 K , 1 atm

This curve was fitted with the theoretical model and the following values were obtained:

$$\sigma = 0.7818 + 15.8246\left(1-\exp-\frac{t}{0.1385}\right) + 5.0998\left(1-\exp-\frac{t}{2.5598}\right) \tag{17}$$

From these fitting values the mobility of the electrons is higher than that of the holes and the time constant is higher for the holes than for the electrons.
The experimental curve for the photoconductivity after the incident laser light is off is shown in figure 6.
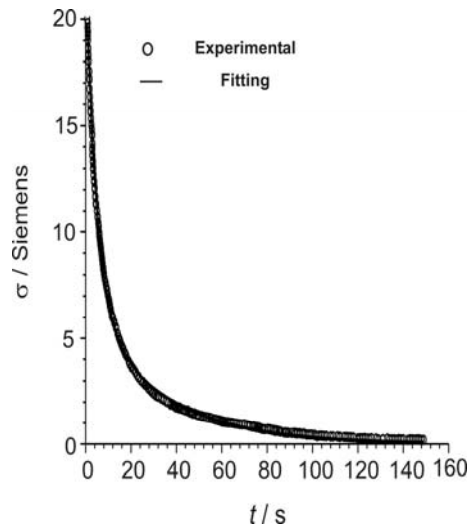
Figure 6. Conductivity transient of the sample with the laser off, at 293 K , 1 atm

This curve was fitted with the theoretical model giving the following result:

$$\sigma = 1.4744 + 14.1178\exp-\frac{t}{4.106} + 7.7292\exp-\frac{t}{24.5977} \qquad (\textbf{18})$$

The experimental data are in very good agreement with the theoretical model. A similar behaviour is observed when the sample is irradiated with white light.

The observed photocurrent is directly proportional to the laser power (Figure 7), measured at the saturation point (from 0 to 10mW, 265 K, 4 n A / m W slope).

Variable wavelength illumination (250 nm to 2000 nm, from the simple monochromator) at room temperature and atmospheric pressure shows a gradual current increase to the saturation level, being larger in the visible spectrum than in the
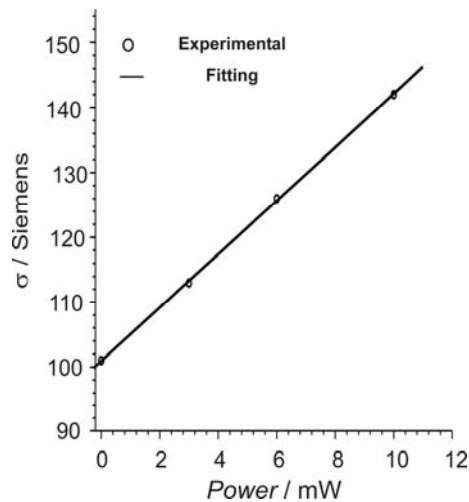

Figure 7. Effect of the laser power upon conductivity of the sample

infrared region. The system discharges to the original level when the irradiation ends. The response time and the time required for saturation depends on the radiation density utilized.

The material also responds to the pressure, showing lower conductivity when vacuum is applied (Figure 8), as expected.
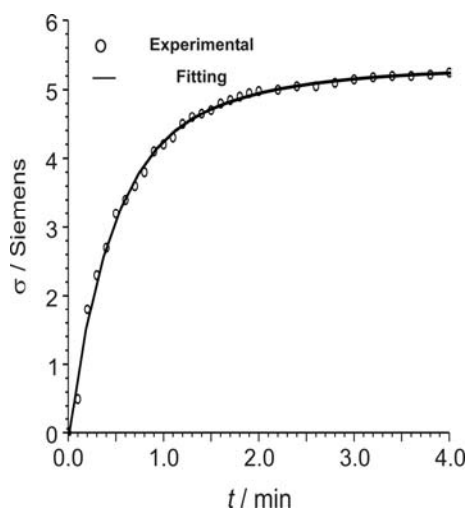

Figure 8. Conductivity transient while illuminating the sample with laser light at 293 K under vacuum

This curve was fitted with the theoretical model giving the equation (19):

$$\sigma = 3.8763 \exp-\frac{t}{0.4143} + 1.5441 \exp-\frac{t}{1.3252} \tag{19}$$

Conductivity increases when air is introduced up to atmospheric pressure. A similar behaviour is observed when Ar or N_2 are introduced to the sample, showing a different value for each gas and these measurements can be calibrated as a gas sensor. The conductivity response with sound application is small (due to the low power used) being more sensitive in the 60 Hz to 40 Hz. frequency range.

The proposed structure of Polyveratrole corresponds to trimeric hexamethoxy-triphenylene radical cation units [1, 2] that have laminar packing, as an ordered columnar phase system (discotic liquid crystal) analogous to that proposed for 2,3,6,7,10,11 hexamethoxy-triphenylene [8]. Conductivity of the material is expected to be linear along the columns (the radical cations would have parallel triphenylene rings and the BF_4^- counter ions packed compensating the positive charge of the cation radical). The behaviour of conductivity as a function of temperature, reflects ionic diffusional aspects and the proposed phase transitions with temperature and pressure, implies relative movements of the triphenylene rings giving better or worse conductivity orientation. All temperature phase transitions are perfectly reversible. The high-pressure phase transition leads to a vitreous system that freezes the high-pressure phase. Heating could reverse this quasi-stable phase at normal pressure. Light irradiation produces charge carriers (probably electron- hole pairs) with concentrations dependent on the radiation frequency, radiation density and the

temperature. Carrier concentration reaches a saturation point as long as the irradiation is maintained (faster with higher temperature, higher frequency and higher radiation density) and it is consumed when the radiation is turned off, while current flows through the circuit, and returns to the original value of conductivity. The behaviour observed at values of pressure close to atmospheric pressure shows that the material is sensitive to the compactness and the relative distance of the triphenylene rings. This piezoelectric behaviour with sound is frequency dependent, perhaps due to a resonance effect of the solid that allows a greater energy absorption in the 40 Hz to 60 Hz frequency range.

The proposed phase changes occur at low temperatures, indicating low activation energy reversible processes. Assuming the polyveratrole structure as a discotic stacking of hexamethoxy-triphynelene units, the phase transitions could involve lateral displacements of these units involving reordering of the counterion (BF_4^-).

Optical absorption measurements

The band gap energy is one of the most important parameters to characterize semi conducting properties. To determine this parameter of Polyveratrole, a thin film (50 μ over ITO) was deposited. The absorption coefficient, **α**, was determined from the experimental transmittance T using equation 20.

$$T = \frac{(1-R)}{1-R^2} \frac{e^{-\alpha t}}{e^{-2\alpha t}} \tag{20}$$

where R is the reflectivity and t the thickness of the film. The contribution of R (is small) was taken into account by subtracting the background to cero. The dependence of **α** upon the photon energy, E, can be written as:

$$(\alpha E) = A(E - E_g)^n \tag{21}$$

Where n =1/2 and n = 2 correspond to the direct and indirect band gap, respectively. The fit of the spectra on figure 1 was for a direct band gap semiconductor with $E_g = 2.41$ eV as shown in figures 9 and 10.
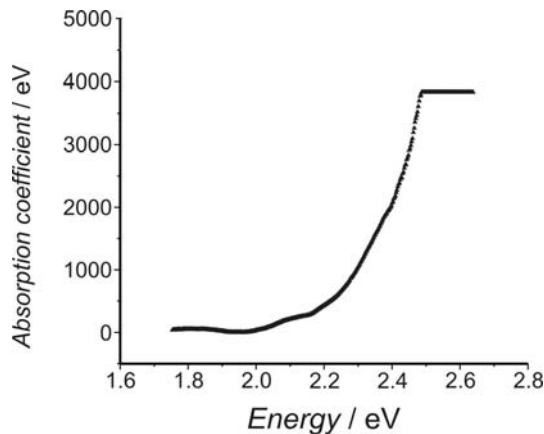

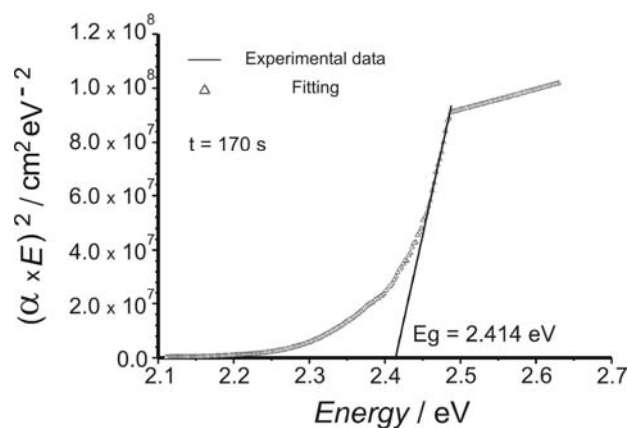**Figure 9.** Absorption spectra at room temperature of polyveratrole

Figure 10. Plots of $(\alpha E)^2$, versus photon energy. The intercept point at the energy axis gives the band gap energy E_g.of the material

Conclusions

The change of conductivity of the material with pressure, temperature and irradiation implies possible structural changes (phase transitions) that sensibly modify that property. Changes in the relative position in the laminar and columnar structure of the trimeric basic units proposed for this material is compatible with the observations under pressure (piezoelectric) and with the temperature. The photoconductivity is produced by the creation of electron -hole current carriers. This compound has potential applications for solar battery and pressure sensor as well as a sound sensor. The band gap of Polyveratrole was found to be 2.41 eV.

References

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