



Electrical conduction study in Polyvinylalcohol and Polyvinylchloride doped by the Ruthenium Terpyridine complex

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Abstract

The object of this work is to study the electrical conductivity of the polyvinylalcohol (PVA) and polyvinylchloride (PVC) polymers doped by a Ruthenium Terpyridine Complex. The analysis of current density as a function of the electrical fields at various temperatures, shows an ohmic conduction at low electric field. Elsewhere, the temperature dependence of the electrical conductivity suggests a change of the conduction mechanism only in PVA-Ru(Terpy)Cl₃ material. The activation energy is markedly changed from 0.350 eV to 0.021 eV at around 285K; this phenomenon is not observed in the PVC-Ru(Terpy)Cl₃ case.

Keywords: Electrical conductivity, PVA-Ru(Terpy)Cl₃, PVC-Ru(Terpy)Cl₃, Absorption spectra, Activation energy.

1. Introduction

The organic polymers present an important material in current industry. The electrical conduction has been made the subject of many experimental studies [1–5]. A development of conducting polymer contributes in variety of applications such as, electroluminescence [6, 7], optical amplifiers [8, 9] and organic transistors [10, 11].

The aim of this work is to analyze the electrical conductivity in the doped films (PVA and PVC) Ru(Terpy)Cl₃ compound. The choice of this compound is based on the following observations.

The 4d⁶ configuration of Ruthenium and the existence of some orbital in the terpyridine molecule conduce to an electronic charge transfer from metal to the ligands [12]. Then, the PVC polymer is polar material, the dipole orientation provokes a relaxation process conducting to the perturbation of conduction phenomena [13]. In fact, by injecting the electron in polymeric chain PVC from metallic cathode, it has been shown a hopping conduction mechanism [14]. Elsewhere, the PVA polymer is a material with polarity bellow than PVC, but it's known that this material can easily associated by hydrogen bonding, with some doped organic molecules [15–20]. The association by hydrogen bond contribute to a charge transfer in the doped film. Finally, some others [21–23] have been interested to use a polymeric films such polyvinyl pyridine in which, they have fixed the Ru(Terpy)₂ complex in order to analyse the photocurrent.

The objective of this work is to study the electrical conduction mechanism in doped PVA and PVC polymers. This phenomenon is discussed and analyzed in each case of the PVA-Ru(Terpy)Cl₃ and PVC-Ru(Terpy)Cl₃ materials.

2. Experimental Section

2.1. Preparation of the Ruthenium Terpyridine complex (Ru(Terpy)Cl₃)

Solution containing 20ml of absolute alcohol, 33 mg of (RuCl₃, 3H₂O) powder and 30 mg of terpyridine (figure1-commercial-Fluka) were reported at reflux during 3 hours. The obtained hasty is rinsed by ethylic - ether gives the final compound.

2.2. Preparation of the PVA-Ru(Terpy)Cl₃ and PVC-Ru(Terpy)Cl₃ materials

The PVA film (-CH₂-CHOH-)_n, 110 μm thick was prepared by dissociating 10 g of PVA disc in 90cm³ of distilled water. The solution is pouting on at ebullition during 30 mn. Then, the liquid solution is displayed on the Plexiglas's plate and placed in the four during one day. The obtained film is rigid transparent. The doping of the PVA by Ru(Terpy)Cl₃ complex is effected during the film elaboration by introducing a concentration in ethanol (used as transfer solvent in PVA) almost equal to 10⁻³ mol/l. In commercial PVC film (-CHCl-CH₂-)_n case, the same concentration in n-butylchlorid (transfer solvent) was poured on the film.

2.3. Spectroscopic measurement

The used technique and absorption measurement has been described earlier [24]. The solvents are of spectroscopy grad were used as received.

2.4. Electrical conduction

The apparatus used to measure the conduction a current is composed of a power supply, keighley electrometer and test cell. The test cell contains a measuring electrode, the counter electrode and guard ring. The current as a function of time was transferred to the personal computer. The effective geometric area of electrodes was 2.3 cm².

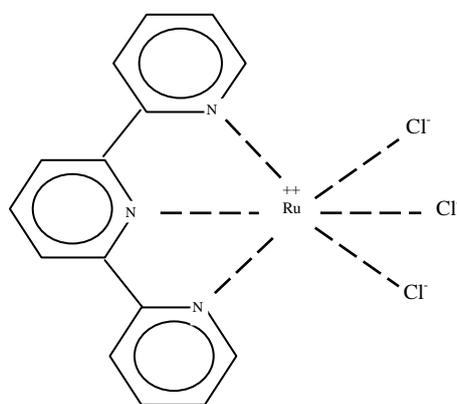


Figure 1: Complex of Ru(Terpy)Cl₃

3. Results and discussion

3.1. UV-Visible Spectroscopy

In this work, the preliminary spectroscopy study justify the choice of the Ru(Terpy)Cl₃ complex such as a compound for studying the conduction in PVA and PVC polymers. In fact, in figure 2 the absorption spectra of the terpyridine molecule and the Ru(Terpy)Cl₃ complex in ethanol are compared at room temperature.

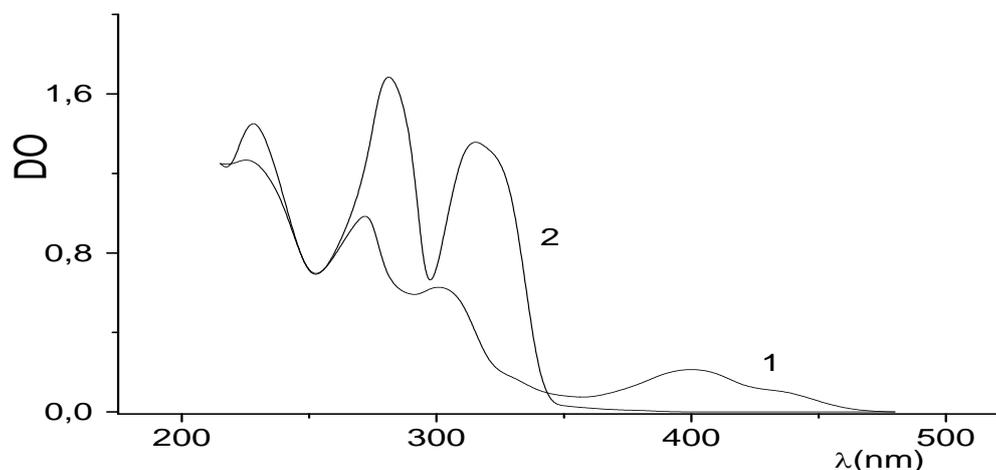


Figure 2: Absorption spectra of the terpyridine (2) molecule and Ruthenium terpyridine complex (1) in ethanol.

The absorption band of Terpyridine appears as well structured, triple-peaked transition respectively at 225 nm, 270 nm and 308 nm. This triple-peaked absorption band is assigned to ($\pi \rightarrow \pi^*$) transition. However, in the Ru(Terpy)Cl₃ complex, a low intensity absorption band appears at 390nm on long wavelength tail of the intense $\pi \rightarrow \pi^*$ terpyridine absorption band. This transition is attributed to charge transfer state from the metal to terpyridine ligands. The charge transfer phenomena is characterized by a new band while is often the longest wavelength transition of the molecule containing nonbonding (n) electrons and is almost always lower in energy than ($\pi \rightarrow \pi^*$) transition.

The charge transfer can be explained by the mechanism in which some of the lone electron pair on nitrogen is committed with σ bonding of the metallic atom in chelating process. The apparition of $d \rightarrow d^*$ transition is possible because Ru has a d^6 configuration and in presence of azaaromatic ligands, a charge transfer can be done from the metal to ligands or from the ligands to metal.

3.2. Electrical conduction

When ions are hopping by a thermally activated process, current density J is expressed as Eq. (1):

$$J = 2nav \exp(-U/kT) \sinh(eEa/2kT), \quad (1)$$

where e , n , a , v , U , k , and T are the charge of electron, carrier density, hopping distance, attempt to escape frequency, activation energy, Boltzmann constant, and absolute temperature. This expression proposed first by Mott and Gurney [25] can be modified as Eq. (2) at high electric fields [26]:

$$J = nav \exp(-U/kT) \exp(eEa/2kT), \quad (2)$$

In Eq. (2), $\exp(-U/kT)$ is independent of the electric field and can be treated as a constant with respect to electric field. It is also an intercept in a $\log J$ vs E plot.

To examine whether or not the conduction process changes, the current density of doped PVA and PVC was plotted as a function of the electric field at three different temperatures (figures 3a and 3b).

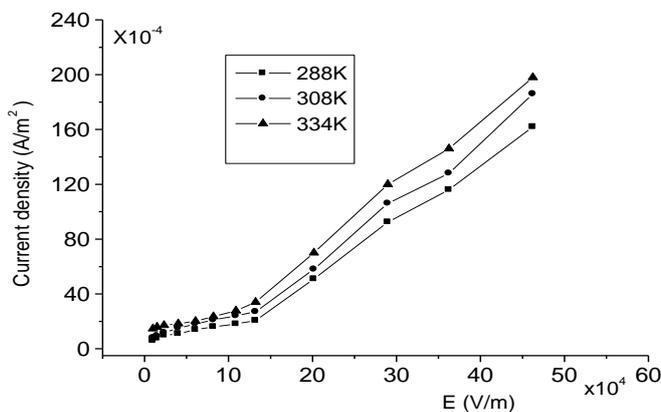


Figure 3a: Current density as a function of electrical Fields at various temperatures in PVA-Ru(Terpy)Cl₃

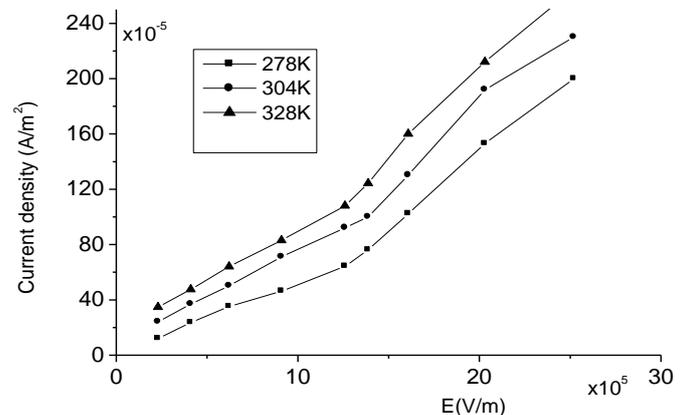


Figure 3b: Current density as a function of electrical Fields at various temperatures in PVC-Ru(Terpy)Cl₃

These figures show that if electric fields is below 10^5 Vm^{-1} for PVA-Ru(Terpy)Cl₃ and below 10^6 Vm^{-1} for PVC-Ru(Terpy)Cl₃, ohmic conduction is observed. However, at high fields in excess of 10^5 Vm^{-1} and 10^6 Vm^{-1} respectively for these doped films, non ohmic conduction is observed. The isochronal current density (j) increases with the increase of electric field (E) at these temperatures. The suppression of the state of change of current density in function of electric fields was found frequently in some polymers [3, 4]. The non linearity observed in this figure implies that the conduction mechanism did change at high fields. From these observation results it is considered that the dominant conduction mechanism at these temperatures is a Schottky effect [24, 27]. In this latter situation some factors can have influenced the mechanism. In fact, it is known that the

electrode material effect displayed an important role in change of the current. Further; the impurities such as the reaction residuals and moisture (structure change, relaxation phenomenon) contributed in the perturbation of the conduction in polymers.

Both Schottky and Poole–Frenkel mechanisms were also examined as follows. The Schottky mechanism is an electrode-limited conduction process and can be expressed by the following equation [28]:

$$J = AT^2 \exp(-\phi/kT) \exp(\beta_S E^{1/2}/kT), \quad (3)$$

$$\beta_S = (e^3/4\pi\epsilon\epsilon_0)^{1/2}, \quad (4)$$

where J , ϕ , β_S , ϵ , and ϵ_0 are the current density, barrier height between the electrode and sample, Schottky coefficient, relative permittivity, and permittivity in vacuum. The Poole-Frenkel mechanism can be expressed by the following equations [22]:

$$\sigma = \sigma_0 \exp(\beta_{PF} E^{1/2}/kT), \quad (5)$$

$$\beta_{PF} = (e^3/\pi\epsilon\epsilon_0)^{1/2}, \quad (6)$$

Where σ and β_{PF} are the conductivity and Poole-Frenkel coefficient; the method to use these equations for the examination of conduction mechanisms is as follows: First, one obtains the coefficients from the slope of $\log J$ vs $E^{1/2}$ plots in the case of Schottky mechanism and $\log \sigma$ vs $E^{1/2}$ in the case of Poole-Frenkel mechanism. Then, the dielectric constants of the sample are estimated from these coefficients. If these relative permittivities agree with the literature values, it can be said that the sample follows the corresponding conduction mechanisms.

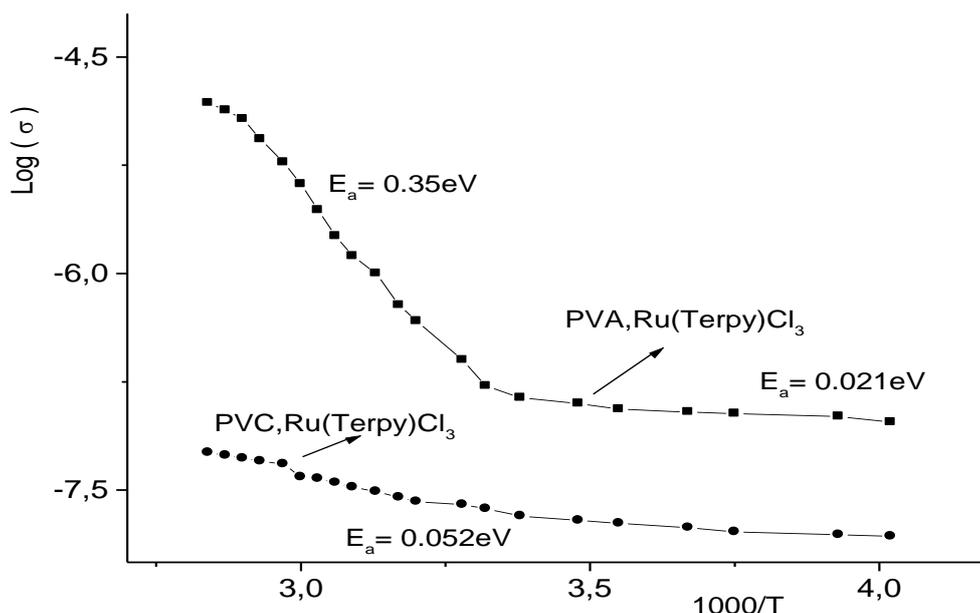


Figure 4: The dependence conductivity of the temperature of PVA-Ru(Terpy)Cl₃ and PVC- Ru(Terpy)Cl₃.

Figure 4 shows the conductivity of PVA-Ru(Terpy)Cl₃ and PVC-Ru(Terpy)Cl₃ as a function of temperature. From this figure, it can be observed that the conductivity increases as a function of decreasing of temperature specially in the PVA, Ru(Terpy)Cl₃ compound. The linear relationship in this figure indicates activation type behaviour of conductivity with the change of temperature. The activation energy E_a equal to 0.350 eV, which was evaluated by fitting the Arrhenius plot of conductivity, is markedly changed from 0.350 eV to 0.021eV at around 285 K suggesting the change of conduction mechanism at this temperature.

The activation energy at high temperature range ($T \geq 285$ K) is due to an electronic transfer from the metallic orbital to the ligands of terpyridine molecular orbital and an electronic transfer between the metallic orbital of the Ruthenium. However, at the temperature below 285K, only the electronic transfer from the metallic orbital to the terpyridine orbital is considered. While, in the PVC, Ru(Terpy)Cl₃ case, the activation behaviour of

conductivity with the change of temperature but no change on the Arrhenius plot behaviour. The constant activation energy ($E_a = 0.052$ eV) suggest in this range of temperature any change of conduction mechanism. Elsewhere, as is shown in this figure, we note a decreasing of the conductivity on going from PVA-Ru(Terpy)Cl₃ to the PVC-Ru(Terpy)Cl₃. The decreasing conductivity is probably due to some phenomenon such as intermolecular relaxation induced by application of electric field. This phenomenon favours a dipolar reorientation of the C-Cl bond at level of PVC polymer, conducting to dielectric behaviour. This situation is observed in some polymers [23, 29] containing C-Cl or C-Br bonds. Another factor such as the conduction by charge transfer due to the hydrogen bonding between ligands of the molecule and OH of PVA fields can not be neglected, the activation energy is markedly changed from 0.350 eV to 0.021 eV at around 285K; this phenomenon is not observed in the PVC-Ru(Terpy)Cl₃ case. In fact, the conductivity in PVA This phenomenon is not observed in the case of the doped PVC on account of a hydrogen bonding absence. This observation is consistent with previous studies [30-32] where it has been observed that a conductivity enhancement is possible with a number of solvents having two or more polar groups on each molecule. It's likely that the PVA solvent has two effects on the Ru(Terpy)Cl₃; the polarity and the hydrogen bonding.

Conclusion

We have reported in this work some results on the electrical conductivity in doped PVA and PVC by (Ru(Terpy)Cl₃) complex. At various temperatures, an ohmic conduction is observed at low electric fields in the two materials. However, the obtained results show that the temperature effect provokes a change of conductivity mechanism in (PVA-Ru(Terpy)Cl₃) material. The change is marked by a change of activation energy. Which is evaluated by fitting the Arrhenius plot from 0.350 eV to 0.021 eV at around 285K; this phenomenon is not observed in the (PVC-Ru(Terpy)Cl₃) case.

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References

1. Muramoto Y., Mizuno Y., Nagao M., Kosaki M., *Proceedings of the 8th International Symposium on High Voltage Engineering, Yokohama, Japan* (1993) 131.
2. Kim E. J. and Ohki Y., *IEEE Trans. Dielectric Electronic Insulation*, 2 (1995) 74.
3. Akiyama K., Ohki Y., Ikeda M., *Proceedings of the 93rd International Workshop on electrical Insulation, Nagoya, Japan* (1993) 365.
4. Kwang Suh S., Jin Ho Nam and Kee Joe Lim, *J. Appl. Phys.*, 80 (11) (1996) 6333-6335.
5. Kim D. W., Yoshino K., *J. Phys. D: Appl. Phys.*, 33 (2000) 464-471.
6. Fried R. H., Gymer R. W., Holmes A. B., Burroughes J. H., Marks R. N., Taliani C., Bradley D. D. C., Dos Santos D. A., Bredas J. L., Logdlund M., Salaneck W. R., *Nature*, 121 (1999) 397.
7. Cross M., Muller D. C., Nothofer H., Scherf U., Neher D., Brauchle C., Meerholz K., *Nature*, 661 (2000) 405.
8. Haque S. A., Nelson J., *J. Science*, 327 (2010) 1466.
9. Ma H., Jen A. K., Dalton L. R., *Adv. Mater*, 14 (2002) 1339.
10. Kim S., Lee J., *Nano. Lett*, 10 (2010) 2884.
11. Ling M. M., Bao Z., *Chem. Mater*, 16 (2004) 4824.
12. Day P., Sanders N., *J. Chem. Soc. A*, (1967) 1536-1541.
13. Decossas F., Moliton A., Marchal E., *J. Polym. Sci.*, 18 (1980) 683.
14. Martin E. H., Hirsch J., *J. Appl. Phys.*, 43 (1972) 1001.
15. Cazeau-Dubroca C., *Trends Phys. Chem.*, 2 (1991) 233-258.
16. Cazeau-Dubroca C., Ayt-Lyazidi S., Cambou P., Peirigua A., Ph Cazeau and Pesquer M., *J. Phys. Chem.*, 93 (1989) 2347.
17. Benali B., Fadouach M., Kabouchi B., Cazeau-Dubroca C., Nouchi G., *J. Mol. Liq.*, 81 (2) (1999) 159-162.
18. Wang Z., Ciselli P., Peijs T., *Nat. Nanotechnol.*, 18 (2007) 1-9.
19. Minus M. L., Chae H. G., Kumar S., *Macromol. Chem. Phys.*, 210 (2009) 1799-1808.
20. Mudigoudra B. S., Masti S. P., Chougale R. B., *Res. J. Engineering. Sci.*, 1(2) (2012) 63-65.
21. Pickup P. G., Murray R. W., *J. Am. Chem. Soc.*, 105 (1983) 4510.

22. Calvert J. M., Schmehl R. H., Sullivan B. P., Facci J. S., Meyer T. J., Murray R. W., *Inorg. Chem.*, 22 (15) (1983) 2151-2162.
23. Gosh P. K., Spiro T. G., *J. Am. Chem. Soc.*, 102 (1980) 5543–5549.
24. Das-Gupta D. K., Joyner K., *J. Phys. D: Appl. Phys.*, 9 (1976) 824.
25. Mott N. F., Gurney R. W., *Electronic Process in Ionic Crystals* (Oxford University Press, London, 1940).
26. Lawson W. G., *Br. J. Appl. Phys.*, 16 (1965) 1805.
27. Das-Gupta D. K., Doughty K., Brockley R. S., *J. Phys. D: Appl. Phys.*, 13 (1980) 2101-2114.
28. O'Dwyer J. J., *The Theory of Electrical Conduction and Breakdown in Solid Dielectrics* (Clarendon, London, 1973).
29. Duroux J. L., Moliton A., Froyer G., Maurice F., *Eur. Polym. J.*, 22 (1986) 439-442.
30. Quyang L., Chu Q., Yang Y., Li G., Shinar, *J. Polymer.*, 45 (2004) 8443.
31. Quyang L., Chu C., Chen F., Xu Q., Yang Y., *Adv. Funct., Mater.*, 15 (2005) 203.
32. Chen C. H., LaRue J. C., Nelson R. D., Kulinsky L., Madou M. J., *J. Applied Polymer Science Published on line Library* (2012).

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