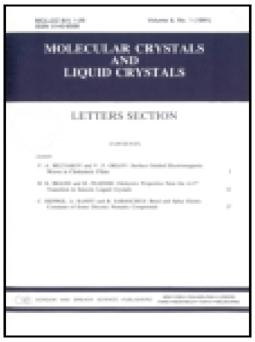

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Study of electrical conduction of polyvinylalcohol films doped by 4-dimethylaminobenzonitrile molecule

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ABSTRACT
Films of pure and doped polyvinylalcohol (PVA) with 4-dimethylaminobenzonitrile (DMABN) molecule are prepared during the development of these films. The effect of UV irradiation and doping on electrical properties of PVA is investigated. We show that the system polymer-molecule has a certain photostability following UV irradiation. The variation of electrical current with temperature show two regions corresponding to different values of activation energy. The activation energies are changed from 0.22 to 0.47 eV, from 0.11 to 0.37 eV and from 0.13 to 0.29 eV for respectively undoped, doped and doped irradiated films. The analysis of I–V characteristics suggests that Schottky emission is the dominant charge transfer mechanism governed by complex of hydrogen bonding.

KEYWORDS
Electrical conductivity; polyvinylalcohol film; 4-dimethylamino benzonitrile; charge transfer; hydrogen bonding; activation energy

1. Introduction

Conductive polymers attracted considerable interest since 1977, when it was shown that the polyacetylene can achieve a high conductivity by a simple doping [1]. Substantial progress has been made after to understand physical and chemical phenomena which can increase the conductivity of the polymers, due to their potential application in optoelectronics and storing information devices. There is a wide variety of organic conductor polymers, for example, the family of polyaniline doped by an inorganic acid [2, 3] exhibits a high conductivity. On the other hand, the significance of finding photonic properties for those materials [4, 5] arises from its important role in some device applications such solar cells [6, 7], light emitting diodes [8], thin film transistors, sensors [9], etc. Special emphasis is put on the polymer-irradiation interaction process, which not only increases electronic mobility but also reduces its potential-barrier giving rise to desired properties of the irradiated polymer. Particular interest has recently attracted by polyvinylalcohol (PVA), because of its excellent physical properties and good charge storage capacity. Doped by metal ions [10–13], physical and electrical properties of PVA can be varied in different degrees. But very little work is available on doped polyvinylalcohol by organic molecules. In this paper, we present, original results concerning the electrical conductivity of PVA doped with 4-dimethylaminobenzonitrile (DMABN). This organic molecule is very polar [14, 15] and exhibits a strong charge transfer (CT) character. The PVA polymer has very important applications due to the role of OH groups [16]. The hydrogen bonding imposes a determined geometrical conformation to DMABN molecule [17].

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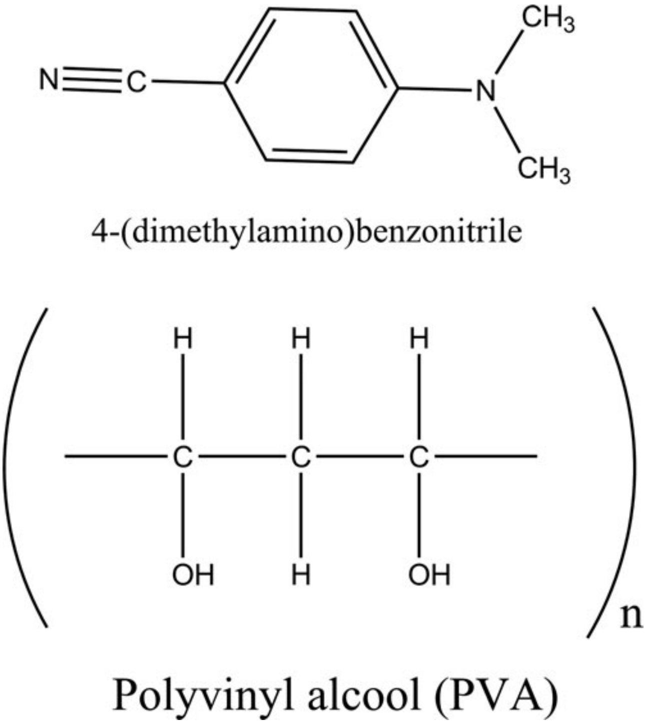

Figure 1. Structure of the polymer and doping molecule.

2. Experimental part

Polyvinylalcohol polymer (PVA) and 4-dimethylaminobenzonitrile (DMABN) are provided from Sigma-Aldrich. The schematic structures of polymer and DMABN of Chemical formula $(CH_3)_2NC_6H_4CN$ are represented in figure 1.

The doping of PVA with DMABN molecule is realized during the elaboration of the film. This latter is obtained by dissolving the polymer powder in distilled water, the solution is boiled for 15 min, after we added a solution of DMABN in ethanol (10^{-2} M) into the PVA solution under stirring. The mixture was displayed on a plate of polymethylmethacrylate and heated about 330K. The films, in the form of disks about 1 cm in diameter, are removed one day after, rigid, transparent and colorless. Films doped and undoped are prepared under the same conditions. The thickness was determined using an electronic comparator. Current was measured with a picoampermeter (model 487 voltage source conduction). Electrical contacts to the sample were two copper electrodes. For the photoconductivity measurements, we use the UV source Low-pressure mercury Analamps with filters to give a wavelength of 312 nm.

3. Results and discussion

3.1. *Doping effect*

Figure 2 shows the variation of the conducting current I with the applied voltage V, at room temperature, for non doped and doped PVA films. Linear I-V plots are obtained in both cases, revealing an ohmic behaviour in which the current density is controlled by generation of charge carriers. In the case of doping, the obtained current values were significantly increased

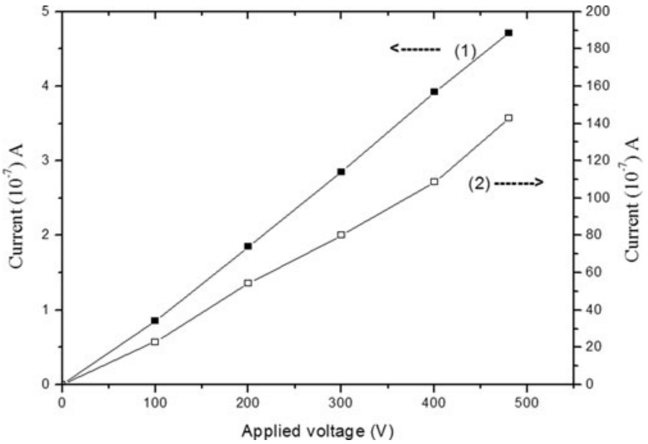

Figure 2. Current as a function of Voltage for PVA(100μm), non doped(1) and doped 10^{-2} M (2).

by a factor of about 40. It's known that PVA can interact by hydrogen bonding with some organic molecules [15, 18, 19].

The association by hydrogen bond contributes to a charge transfer in the doped film. Elsewhere, spectroscopic studies on DMABN in various polymeric media [14] have shown that this very polar molecule of dipole moment $\mu = 7{,}6$ D can strongly interact with the OH group particularly in PVA where the absorption spectrum of this molecule is shifted to lower energies compared to spectra in polyethylene or in polyvinylchloride, polymers not having OH group [20]. According to these works this shift cannot be attributed only to the polarity of the polymer, but also to the formation of complexes by hydrogen bonding between PVA and DMABN. The emission study of this molecule in solution and polymer medium, showed the presence of two fluorescence emitting states, one of them is TICT (Twisted Internal Charge Transfer) state. This latter is favored by a geometric conformation adopted by the molecule DMABN in ground state, during the complexation with the hydrogen bonding OH groups of PVA, which increases the attractor ability of cyanide group in DMABN. The molecule acquires a great dipole moment. Following an electrical excitation, there is creation of an important space charge which facilities the charge transfer along the polymer chain. In measuring the conducting current I as a function of increasing concentration of DMABN (not shown in this paper), at room temperature, for PVA films of 49.18 μm thickness, we observed the increase of the current with the dopant concentration until 10^{-1}M, higher than this concentration, the current tends to a constant value. This phenomena is attributed to the formation of charge transfer complexes, the current stabilization observed beyond this concentration is probably due to the increase of the polarity of the system PVA- DMABN. The mobility of charge carriers is influenced by the dopant concentration, because of forces between dipoles, which can increase or decrease the electronic conduction according to the spatial configuration imposed to DMABN. Similar behavior has been discussed on PVA doped by other molecules [21–22].

To study the transport mechanism in PVA doped films, current-voltage (I–V) characteristics are reported in figure 3.

Figure 3.1 presents Log I vs $V^{1/2}$ for PVA-DMABN system. This plot shows a linear behavior with $V^{1/2}$ at higher voltages, and a slight deviation from linearity at lower voltages. This phenomena can be attributed to the accumulation of space charge at the electrodes. The linear behavior of log I vs $V^{1/2}$ plot points to classic conduction mechanism in which the charge carriers are released by thermal activation over a potential barrier, were electron transit over

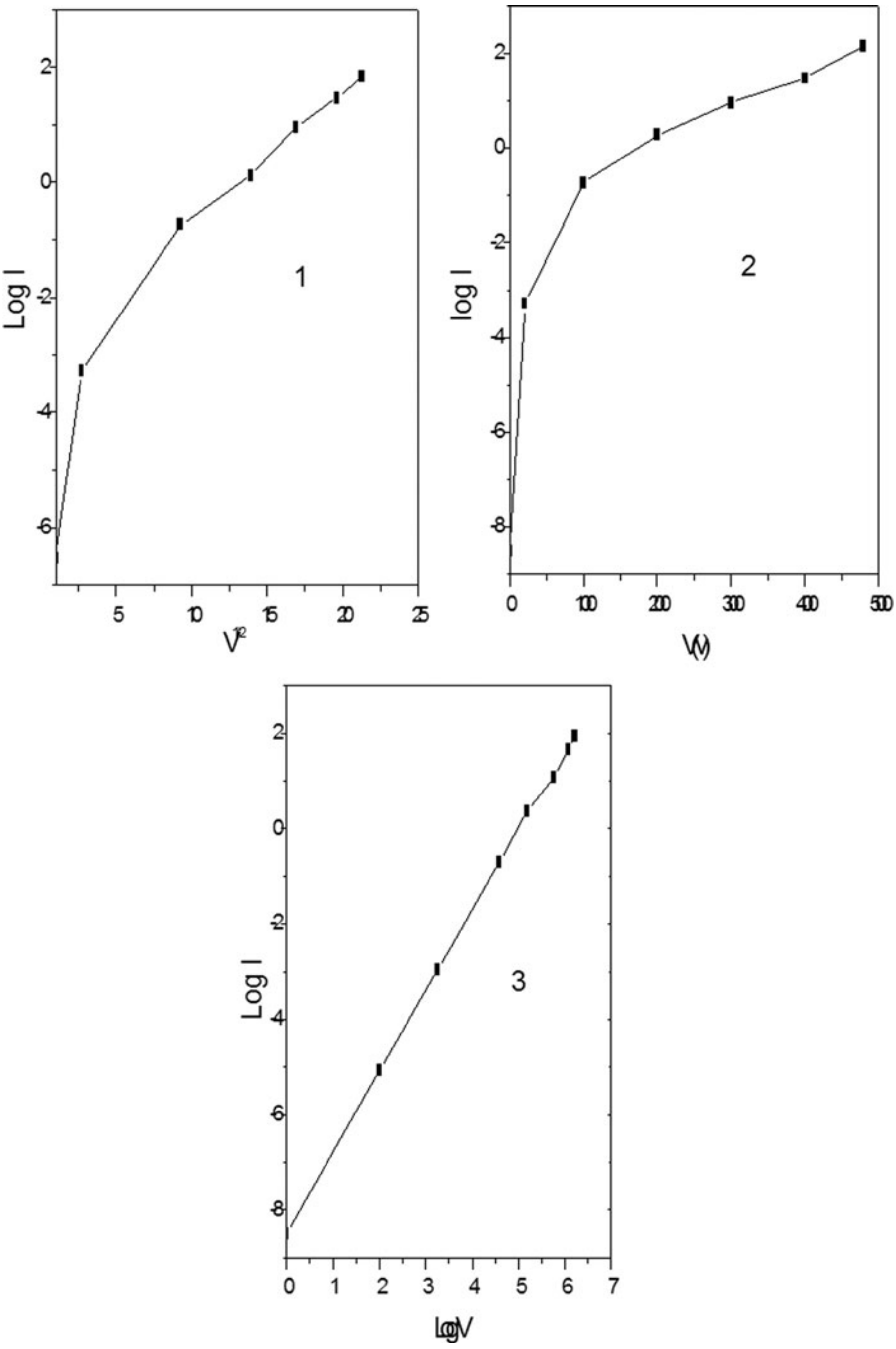

Figure 3. Study of I-V characteristic of the PVA film doped (10^{-2}M), (1):Log I = f($V^{1/2}$), (2):LogI = f(V), (3): Log I = f(LogV).

the barrier between the cathode and the film (Schottky emission) [23]. Alternatively charge carriers can be released from the traps into the polymer chain (Poole–Frenkel effect). To determine the conduction mechanism in our case, we verified if the process is thermally activated, using the Arrhenius relation indicated below. Figure 4 presents the conductivity of PVA isolated and PVC-DMABN as a function of temperature. The plots show some linearity over two

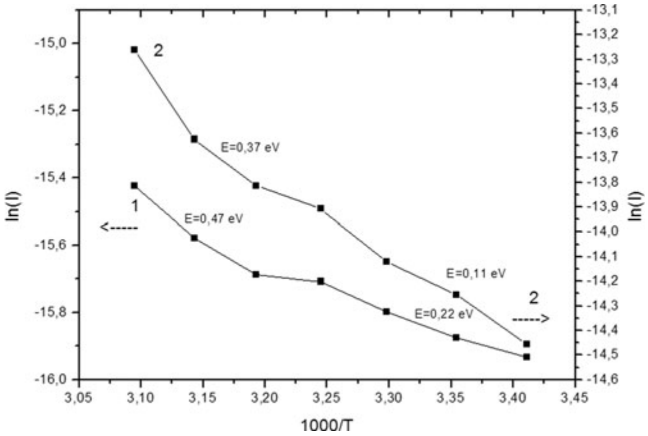

Figure 4. The dependence conductivity of the temperature; (1): undoped film, (2): doped PVA film.

different temperature regions with different slopes in the low and high temperatures regions. The activation energies values can be fitted to the relation $I = I_0 \exp(- Ea / KT)$ where I is the conducing current at the temperature T, I_0 is a constant, Ea is the activation energy and K is the Boltzmann constant. At around 308 K, this energy is changed from 0.22 to 0.47 eV and from 0.11 to 0.37 eV respectively for undoped and doped PVA. This result shows two regions of activation energy with two different types of conduction mechanisms, phenomena which generally observed for polar polymers as PVA and enhanced in case of hydrogen bonding [24–25] between dopant and polymer. Such behavior in I-V plots and the nonlinearity of the curve Log I = f (V) (Fig 3.2) permit us to reject the possibility of conduction by Poole-Frenkel effect [26]

The energy required for conduction from one site to another, which is low for PVA doped, suggests us that the conduction in this film is due to the “Hopping” [26]. The linearity of the curves log I = f (Log V) (Fig 3.3) may confirm the hypothesis of a conduction by “hopping”: where charge carriers can jump from a localized donor state to another, between neighboring sites, over the barrier released by thermal activation according to the Schottky emission [23].

3.2. Effect of irradiation

The PVA and PVA-DMABN films were irradiated with UV (of wavelength 312 nm) at room temperature by the UV lamp to investigate the photocurrent properties. Figure 5 shows the current-voltage characteristics of those films under irradiation.

Irradiated PVA and PVA-DMABN films showed the same ohmic behavior than non irradiated films, but exhibits higher conductivity than latters. In addition for PVA-DMABN we observed a fast increase of the current (Fig. 5), whose can be explained that at the beginning, the conduction is due to the presence of dopant molecule, the effect on UV irradiation result in an increase in the number of charge carriers created. This can be explained on the basis, that irradiation of polymer is to rupture bonds and release more electrons and free radicals which are able to migrate through the polymeric chain resulting to an increasing in electrical conductivity. In addition to this we registered the variation of the conducting current as a function of time at electric fields about $106V.m^{-1}$, for doped and undoped films under irradiation (Fig. 6). It is seen that the current decreasing quickly after a few minutes of the UV lamp switched off. The conducting current of doped films is greater and also tends to a constant value (Fig. 6. 2), but for undoped films, the value of the current tends slowly to zero (Fig. 6.1).

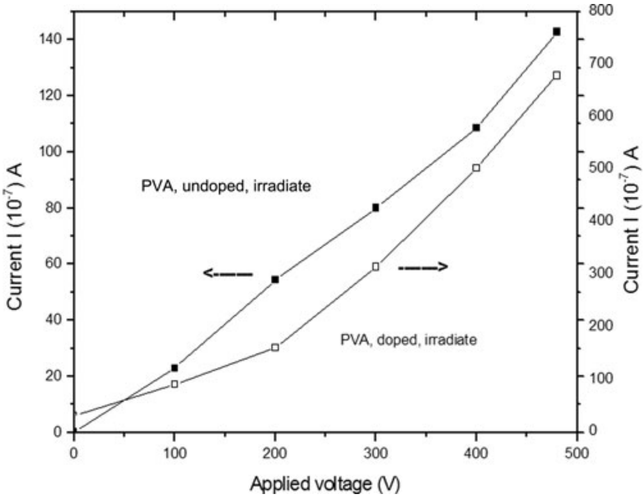

Figure 5. Irradiation effect on the characteristic I = f (V) for undoped PVA (1) and doped PVA (2).

This behavior shows the role of UV photons in the creation of the charge carriers [27–29], called Photoelectret observed for the first time by Nedzhakov, these entities have a longer lifetime in the case of doped polymer, justifying the higher current values. This result is in good agreement with that obtained by Shrivastava et al. [30]. Besides that, the electron-hole separation induced by light leads to CT excited states, which are more delocalized compared to those located at the polymeric chain.

Figure 7 shows the conducting current as a function of temperature. We observed that the current increases as a function of decreasing of temperature. The activation energy Ea for doped and irradiated film, which was evaluated by fitting the Arrhenius plot above, is changed from 0.13 eV to 0.29 eV at around 308 K shows two regions of activation suggests a change of the conduction mechanism at this temperature. The activation energy is lower under irradiation, showing that the conduction is essentially electronic.

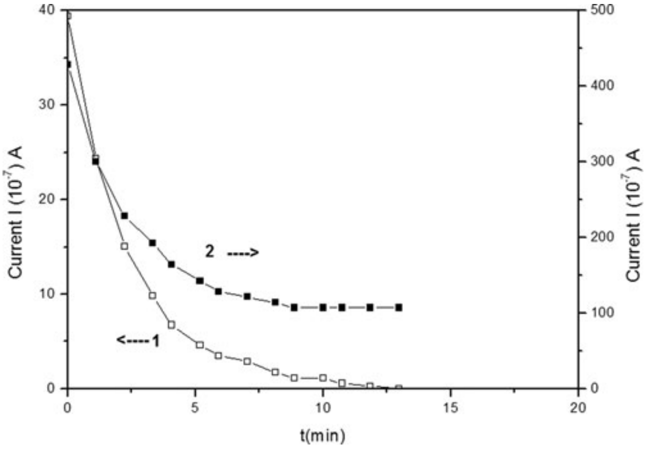

Figure 6. Current as a function of time for doped PVA after the lamp UV was swished off.

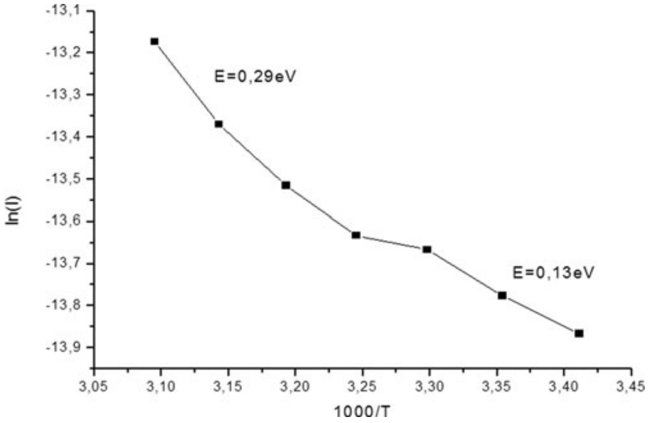

Figure 7. The dependence conducting current of the temperature for doped and irradiate film.

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Conclusion

In this work, we doped polyvinylalcohol (PVA) with 4-dimethylaminobenzonitrile (DMABN), polar molecule, to enhance its electrical conductivity. This enhancement has been explained on the basis of charge transfer complex formation, due to the presence of hydrogen bonds between polymer and dopant. Studies of current-voltage characteristics suggested that Schottky emission is the dominant charge transport mechanism operating in both undoped and doped films, with a low activation energy. This latter is evaluated from 0.37 eV to 0.11 eV for doped PVA at around 308 K. Irradiated and doped films gives optimum values for the electrical properties. No change in conductivity mechanism was observed for the PVA films doped and irradiated with UV (of wavelength 312 nm) at room temperature, inducing that PVA is a photostable material under these conditions.

References

[1] Margolis, M. (1989). *Conductive Polymers and Plastics*, Chapman and Hall, London.
[2] Epstein, A. J., Ginder, M., Zuo, F., Woo, H. S., Tanner, D. B., Richter, A. F., Angelopoulos, M., Huang, W. S., & MacDiarmid, A. G. (1987). *Synthetic Metals*, *21*, 63–70.
[3] Kumar, N., Vadera, S. R., & Jana, P. C. (1992). *Polymer*, *33*, 2424.
[4] Kwon, J. H., An, J. Y., Jang, H., Choi, S., Chung, D. S., Lee, M. J., Cha, H. J., Park, J. H., Park, C. E., & Kim, Y. H. (2011). *Journal of Polymer Science Part A: Polymer Chemistry*, *49*, 1119–1128.
[5] Anuragudom, P., El-daye, J., Chinwangso, P., Advincula, R. C., Phanichphant, S., & Lee, T. R. (2011). *Polymer International*, *60*, 660–665.
[6] Yakuphanoglu, F. (2010). *Journal of Alloys and Compounds*, *494*, 451–455.
[7] Haldar, A., Maity, S., & Manik, N. B. (2008). *Ionics*, *14*, 427–432.
[8] Tamilavan, V., Sakthivel, P., Li, Y., Song, M., Kim, C. H., Jin, S. H., & Hyun, M. H. (2010). *Journal of Polymer Science Part A: Polymer Chemistry*, *48*, 3169–3177.
[9] Du, J. F., Bai, Y., Chu, W. Y., & Qiao, L. J. (2011). *Journal of Applied Electrochemistry*, *41*, 183–187.
[10] Gökçen, M., Tunç, T., Altındal, Ş., & Uslu, İ. (2012). *Materials Science and Engineering: B*, *177*, 416–420.

[11] Devikala, S., Kamaraj, P., & Arthanareswari, M. (2013). *International Research Journal of Pure & Aplied Chemistry*, *3*, 257–263.

[12] Lazar, Z., Benali, B., Elblidi, K., Addou, M., Kabouchi, B., Cazeau-Dubroca, C., Dordor, P., & Nlate, S. (2002). *Ph. Cazeau, Phys. Chem. News*, *8*, 51–54.

[13] Devikala, S., Kamaraj, P., & Arthanareeswari, M. (2013). *International Research Journal of Pure & Applied Chemistry*, *3*, 257–263.

[14] Cazeau-Dubroca, C., lyazidi, S.Ait, Nouchi, G., & Peirigua, A. (1986). *Ph. Cazeau, Nouv. J. Chem.*, *10*, 337.

[15] Cazeau-Dubroca, C. (1991). *Trends in Phys.Chem.*, *2*, 233.

[16] Tawansi, A., El-Khodary, A., & Abdelnaby, M. M. (2005). *Current Applied Physics*, *5*, 572–578.

[17] Kadiri, A., Martinaud, M., & Cazeau-Dubroca, C. (1991). *Chem. Phys. Lett.*, *65*, 484.

[18] Wang, Z., Ciselli, P., & Peijs, T. (2007). *Nat. Nanotechnol.*, *18*, 1–9.

[19] Minus, M. L., Chae, H. G., & Kumar, S. (2009). *Macromol. Chem. Phys.*, *210*, 1799–1808.

[20] Cazeau-Dubroca, C., Ayt-Lyazidi, S., Cambou, P., Peirigua, A., Cazeau, P. H., & Pesquer, M. (1989). *J. Phys. Chem.*, *93*, 2347.

[21] Migahed, M. D., Tawansi, A., & Bakr, N. A. (1982). *European Polymer J.*, *18*, 975–980.

[22] Uma Devi, C., Sharma, A. K, & Rao, V. V. R. N (2002). *Materials Letters*, *56*, 167–174.

[23] Mott, N. F., & Gurney, R. W. (1940). *Electronic Processes in Ionic Crystals*, Oxford University. Press, London.

[24] Quyang, L., Chu, Q., Yang, Y., & Li, G. (2004). *Shinar, J. Polymer.*, *45*, 8443.

[25] Chen, C. H., LaRue, J. C., Nelson, R. D., Kulinsky, L., & Madou, M. J. (2012). *J. Applied Polymer Science*, 125(4), 3134–3141.

[26] Hill, R. M. (1971). *Phil. Mag.*, *23*, 59.

[27] Quamara, J. K., Pillai, P. K. C., & Sharma, B. L. (1982). *Acta Polym.*, *33*, 501.

[28] Fridkim, V. M., & Zheludev, I. S. (1961). *Photoelectrects and Electo Photographic Process*, Consultant Bureau Inc., New York, *15*.

[29] Burland, D. M., & Schein, L. B. (1986). *Physics Today*, *39*(5), 46–61.

[30] Shrivastava, S. K., Ranade, J. D., & Shrivastava, A. P. (1979). *Phys. Lett.*, *72*, 195.