Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Der Pharmacia Lettre, 2011, 3 (6):250-256
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0974-248X
USA CODEN: DPLEB4

Synthesis and Electrical Conductance Studies of o-Aminophenol - Melamine-Formaldehyde Copolymer

W. B. Gurnule[1*] and Deepti B. Patle[2]

[1]Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur, India
[2]Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukdoji Maharaj, Nagpur University, Nagpur, India

---

ABSTRACT

The present paper reports the electrical conductivity study of a copolymer resin. The resin o-aminophenol (o-AP) - melamine (M) - formaldehyde (F) was synthesized by the condensation of o-aminophenol and melamine with formaldehyde in the presence of a hydrochloric acid catalyst with 1:1:3 molar ratio of reacting monomers. Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the copolymer resin. The electrical properties of o-APMF copolymer resin were measured over a wide range of temperature (314-425 K). From the electrical conductivity of this copolymer resin, activation energy of electrical conduction has been evaluated and was found to be 13.65 x 10^{-20} J/K. The electrical conductivity of the copolymer resin was found to be lies in the range of 1.69 x 10^{-10} to 4.4 x 10^{-9} ohm^{-1} cm^{-1}. The plot of log σ vs. 10^3 / T was found to be linear over a wide range of temperature, which indicates that the Wilson's exponential law $\sigma = \sigma_0 \, exp^{(-\frac{Ea}{KT})}$ is obeyed. On the basis of above studies this copolymer can be ranked as semiconductor. When a voltage is applied to a thin film of this copolymer resin then it has emitted light. This remarkable property of this copolymer resin may be used to make a wide range of semiconducting and electronic devices such as transistors, light emitting diodes, solar cells and even lasers which can be manufactured by much simpler way than conventional inorganic semiconductors.

Keywords: Synthesis, o-APMF, semiconductors, copolymer, electrical conductivity.

INTRODUCTION

Semiconductor materials are the foundation of modern electronics, including radio, computers, telephones, and many other devices. Such devices include transistors, solar cells, many kinds of diodes including the light-emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits. The copolymers are well known for their behavior as semiconductors. Although a variety of conjugated organic molecules are known as semiconductors, the carrier mobility in them is usually low. This is due to the difficulties in, which electrons jumps form one molecule to another and hence, the carrier mobility in the compound of this type increases with increasing molecular size.

Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the copolymer resin by T. K. Pal et. al [1]. In this connection, studies were made to establish a correlation between the chemical structure and characteristics defining semiconducting properties [2]. Work on organic conducting polymers is carried out extensively due to their wide applications [3] in areas such as chemically modified electrodes, sensors etc. Perkin and Kolosonov [4] have studied the electrical conductivity of phenol-formaldehyde resin. An industrially useful semiconducting material has been reported by Dewar et.al.[5]. The conductivity of o-aminophenol-melamine-formaldehyde copolymer resins have been reported over a wide range of temperature [6].

Work on organic conducting polymers is carried out extensively due to their wide applications [7] in areas such as chemically modified electrodes, sensors etc. Patel and Manavalan [8] reported the electrical properties of p-hydroxybenzoic acid-thioureatrioxane copolymer. The electrical resistivities of 2-hydrexyaceto-phenoneoxime-thioureatrioxane resin were reported and these polymers are ranked as semiconductors [9-10]. A new family of chemically amplified positive resists based on methacrylate copolymers has been developed by R. D. Allen et.al.[11]. Newberg, C. and Baumgartner B. [12] studied the electrical properties of polymeric materials that can be used for gloves and finger cots. Singru et.al reported the semiconductive copolymers synthesized by 8-hydroxyquinoline5-sulphonic acid and oxamide (O) with formaldehyde (F) and studied their AC and DC conductivity [13]. Dhanraj T. Masram and coworkers reported the conducting polymers predicted to be the futuristic materials for the development of light emitting diodes, antistatic and EMI materials, sensors, optoelectronic devices and rechargeable batteries due to their unique conduction mechanism and greater environmental stability [14]. Since delocalized electrons and conjugation impart semiconducting properties to compounds, the present study deals with synthesis, structural characterization of a new copolymer synthesized from o-aminophenol, melamine with formaldehyde and its electrical conductivity measurement study.

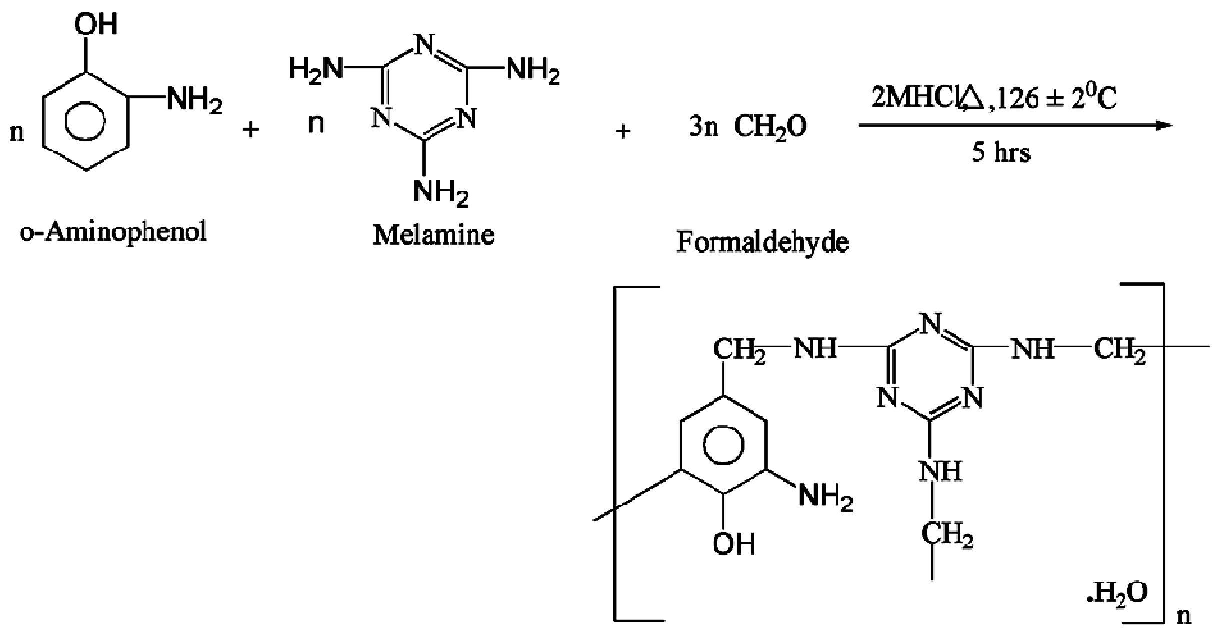
MATERIALS AND METHODS

o-Aminophenol, melamine and formaldehyde (37%) were of analytical grade and chemically pure, (all from Merck India) and wherever necessary the purity was tested and confirmed by thin layer chromatography using Silica gel as stationary phase and chloroform: methanol (9:1). Solvents like N, N′- dimethyl formamide and dimethyl sulphoxide were used after distillation.

Synthetic procedure of o-APMF copolymer resin

The o-APMF copolymer resin was prepared by the condensation polymerization of o-aminophenol (0.1mol) and melamine (0.1mol) with formaldehyde (0.3mol) in hydrochloric acid medium at 126 ± 2 °C in an oil bath for 5 h. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of o-aminophenol - formaldehyde copolymer, which might be present along with the o-APMF copolymer.

The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1(v/v) HCl/water. This process was repeated twice to separate the pure copolymer. The resulting polymer sample washed with boiling water and dried in vacuum at room temperature. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these copolymer resins found to be 87%. The sieved resin was used for further characterization. The reaction sequence of the synthesis of o-APMF copolymer resin is shown in Scheme 1.



Scheme1. Formation and suggested structure of o-APMF copolymer resin

Conductivity Measurement
Experimental Techniques

The DC electrical conductivity measurements in solid state was carried out in a suitable sample holder designed for the purpose, in the temperature range of 313K to 463K at constant voltage of 50 volts across the pellet prepared from copolymer resin. The measurements were made by Auto Compact LCR-Q tester model 4910.

(1) Preparation of Pellet

The copolymer sample was dried properly and thoroughly ground to a fine powder in agate mortar and pestle. The pellet was prepared of the well powdered copolymer resin isotectically in a steel die at under a pressure of 10 metric tons cm^{-2} with the help of hydraulic press.

(2) Measurement of DC electrical resistivity

a. Sample holder:

The pellet of copolymer resin sample was mounted between the two brass electrodes.

b. Furnace for heating the sample:

For measurement of resistivity at different temperatures, a suitable digital muffle furnace embedded with high grade glass wool after single line brick lining and Alumel-Chromel thermocouple up to 1200ºC having heating control regulator, was used. The current supplied to the furnace was recorded by means of AC ammeter. The pellet fitted in the sample holder is kept in the furnace. The connecting wires of two electrodes of the sample holder were taken out for the connection.

c. Data recording:

The connecting wires from the sample holder kept in the furnace, were connected to the terminals of LCR-Q tester model 4910. In this way corresponding resistances of the pellet at various temperature was measured directly. The temperature of the digital furnace slowly increases and resistance is noted on LCR meter, nearly from temperature range 30ºC to 190ºC

RESULTS AND DISCUSSION

The values of electrical conductivity at different temperatures are found to be in the range of 1.48×10^{-09} to 6.4×10^{-12} $ohm^{-1}cm^{-1}$. The thermal activation energy and the values of electrical conductivity at different temperatures are given in Table 1. The resistance values of the pellets of the copolymers ranging from 313 K to 423 K were converted into conductivity values (s) by taking into account the thickness of the pellet and its diameter and evaluating thickness area parameters of the pellet of a particular copolymer. Generally the diameter of the pellet remained constant (1.3 cm) since the same die was used and the thickness varied from 0.254 to 0.272 cm according to the amount of sample present. The temperature dependence of the electrical conductivity of the copolymers is shown in Fig. 2. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation (1) [15].

$$\sigma = \sigma_0 \ \exp.^{\left(-\frac{E_a}{KT}\right)} - - - - (1)$$

where

σ	=	electrical conductivity at temperature T.
σ_0	=	electrical conductivity at room temperature
Ea	=	Activation energy of electrical conduction.
k	=	Boltzmann Constant (0.8625×10^{-4} ev. deg^{-1} or 1.3817×10^{-23} J. $mol.^{-1}K^{-1}$).
T	=	Absolute temperature.

This relation has been modified as,

$$\log\sigma = \log\sigma_0 - \frac{E_a}{2.303KT} - - - - (2)$$

According to this relation, a plot of log σ vs 1000/T would be linear with negative slope. The result of the D. C. conductivities are presented here in the form of plots of log σ vs 1000/T for each set of data, as the range of conductivities was found to be 1.48 x 10^{-09} to 6.4 x 10^{-11} $ohm^{-1}cm^{-1}$.

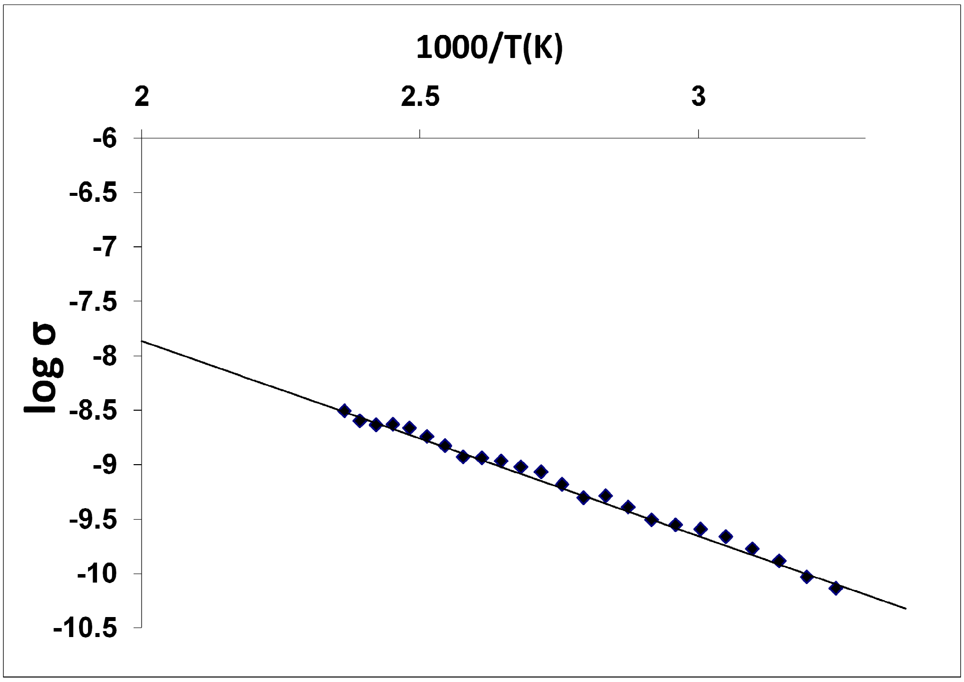


Fig.2. Electrical Conductivity plot of o-APMF Copolymer Resin

It will be seen from the plots (Fig. 1) of copolymers that there is a consistent increase in electrical conductivity as the temperature rises roughly 313 K to 423 K. This trend is a characteristic of semiconduction. The activation energies were determined from the curves log σ vs 1000/T. The plot of log σ vs 1000/T are found to be linear (Fig. 1) over a wide range of temperature, which indicates the semiconducting nature of copolymers. Over the whole temperature range, the values of the electrical conductivity vary between 1.69 x 10^{-10} to 3.1 x 10^{-9} ohm^{-1} cm^{-1}. The conductivities are in the order of 10^{-08} to 10^{-12} $ohm^{-1}cm^{-1}$due to comparatively small intra intermolecular charge transfer of copolymers [16].

From the analysis of our results it can be assumed that the difference in electrical be assumed that the difference in electrical properties of copolymer studied are mainly by their chemical structure, over the whole temperature range the values of the electrical conductivity vary between 1.69 x 10^{-10} to 3.1 x 10^{-9} ohm^{-1} cm^{-1}. The conductivities are in the order of 10^{-9} to 10^{-10} ohm^{-1} cm^{-1} due to comparatively small intra intermolecular charge transfer of copolymer [17-18]. Plastics semiconductors are easier, safer and less expensive to manufactures than conventional semiconductors. Because of the lower cost of manufacturing o-APMF semiconducting copolymer, it may be used as transistors, integrated circuits (IC) for low cost as well as chemical sensors in electronic devices.

Table 1.Electrical conductivity data of o-APMF copolymer

Copolymer	Electrical conductivity 313 K	423 K	ΔT (K)	ΔE (J/K)
o-APMF	1.69×10^{-10}	3.1×10^{-09}	303-423	13.65×10^{-20}

CONCLUSION

From the results of electrical conductivity of these copolymers, the following conclusions can be drawn :

i. The electrical conductivity of o-APMF copolymers at room temperature lies in the range of 1.69×10^{-10} to 3.1×10^{-9} ohm^{-1} cm^{-1}.
ii. The plots of log σ vs 1000/T were found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma_0 \ \exp^{(-\frac{Ea}{KT})}$ is obeyed.
iii. Electrical conductivity of each of these copolymer resins increases with increase in temperature. Hence, these copolymers may be ranked as semiconductors.

The resistance of the polymeric material depends upon incalculable parameters such as porosity, pressure, methods of preparation, atmosphere etc., but these parameters do not affect the activation energy (ΔE) and therefore, it is fairly reproducible. The magnitude of activation energy depends on the number of π-electrons present in the semiconducting material. The more is the number of π -bond, the lower is the magnitude of activation energy and vice-versa.

Acknowledgement
Authors are thankful to the Director, Laxminarayan Institute of Technology, Nagpur, India, for providing the necessary laboratory facilities. One of the author (W.B. Gurnule) thanks to UGC New Delhi for financial assistance.

REFERENCES

[1] W. B. Gurnule, H. D. Juneja, and Paliwal, *Asin J. Chem*., **2000**, 12(1), 51.
[2] E. M. Genies. , A. A. Syed and C. Tsintavis, *Mol. Cryst. Liq. Cryst*., **1985**, 121, 181.
[3] P. S. Lingala, L.J .Paliwal, and H. D. Juneja, National Seminar on Polymers, Chennai, **1999**, 21.
[4] L. A. Perkin, and A.S. Kotaosonow, *Konstr. Materosn Grafita*, **1974**, 8, 122.
[5] J. S. Dewar, and A.M. Talati, *J. Am. Chem. Soc*., **1964**, 86, 1592.
[6] Deepti B. Patle, W. B. Gurnule, A. B. Zade, *Der Pharma Chemica*, **2011**, 3(3), 341-353.
[7] L. Pardeshi, A. Rasheed, and R.A. Bhobe, *J. Ind. Chem. Soc*., **1980**, **57,** 388.
[8] H. B. Pancholi, and M.J Patel. *Indian Chem. Soc*., **1998, 75**, 86.
[9] J. E. Katon, Organic Semiconducting Polymers, Marcel Dekker Inc., New York, **1968.**
[10] P. Yang et al., *Phys. Rev. B*, **2007**, 76, 241201R.
[11] R. D. Allen, G. M. Wallraff, W. D. Hinsberg, L. L. Simpson, and R. R. Kunz, Polymers for Microelectronics, ACS Symposium, (Print): Publication Date - November 23, **1993**, Chapter 11,

pp 165–177 Chapter DOI: 10.1021/bk-1994-0537.ch011 Series, Vol. 537 ISBN13: 9780841227217eISBN: 9780841213937.
[12] C. Newberg, B Baumgartner, Chase R. N. Singru, W. B. Gurnule, A. B. Zade, *Der pharma Chemica*, **2011**, 3 (5), 123-127.
[13] Dhanraj T Masram, *Archives of Applied Science Research*, **2010**, 2 (2):153-161
[14] S.S.Rahangdale, W. B. Gurnule, A. B. Zade, *Int. J. Chem. Sci*., **2009**, 7(2).
[15] A. D. Borker, M. C. Gupta and S. S. Umare, *Polymer-Plastic Technology and Engineering*, **2001**, 40 (2), 225-234.
[16] U. S. Wawre and S. S. Umare, *React. Funct. Polym*, **2005**, 65(3), 343-350.
[17] M. M. Patel, M. A. Kapadia, G. P. Patel and J. D. Joshi, *J. Appl. Polym. Sci*., **2007**, 106(2), 1307 - 1317.