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Archives of Applied Science Research, 2013, 5 (3):153-158 (http://scholarsresearchlibrary.com/archive.html)



Synthesis and electrical conductance study of newly synthesized ligands derived from m-cresol, melamine and formaldeyhyde

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ABSTRACT

Terpolymeric ligand (m-CMF-I and m-CMF-II) synthesized by acid catalyzed polycondensation of m-cresol and melamine with formaldehyde by varied molar proportion of the reacting monomers. The polycondensation was carried out at $120-125^{\circ}$ C in an oil bath in presence of 1M HCl. Structural study was carried out with the help of elemental analysis, IR and NMR. Molecular weight of ligand was determined by non aqueous conductometric titration. In present paper electrical properties of terpolymers were studied. Electrical conductivity was studied as a function of temperature using voltage divider method. Terpolymeric ligands were found to show semiconducting behaviour in different temperature ranges. The activation energy found to be in order m-CMF-I > m-CMF-II.

Keywords: Polycondensation, Terpolymeric Ligands, Activation energy, Electrical conductivity.

INTRODUCTION

Semiconductors have played an extremely vital role in the development of modern electronics; particularly in the communication and computer fields. Plastic semiconductors are easier, safer and less expensive to manufactures than conventional semiconductors. Because of the lower cost of manufacturing 8-HQ5-SAOF semiconducting terpolymer may be used as transistors, integrated circuits (IC) for low cost as well as chemical sensors in electronic devices [1]. Recently it has been reported that the chelate polymers have been used as semiconductors. Polymer metal complexes shows interesting and important characteristics, especially in areas such as semiconductors, molecular recognition, heat resistance and electrical insulation properties [2-4]. In fact conductivity depends upon the external condition such as temperature, humidity, pressure, thickness of sample as well as its chemical structure [5-6]. In this connection, studies were made to establish a correlation with their physical properties and chemical structure. Ingle *et al* recently reported semiconducting behaviour of terpolymer resin-I derived from sulphanilic acid, melamine and formaldehyde.[7]. Masram *et al* reported the synthesis and electrical properties of some resins [8]. Gurnule *et al* studied the electrical conductivity of melamine-formaldehyde copolymer [9]. An industrially useful semiconducting material was reported by Dewar *et al* [10]. Patel and Manavalan reported the electrical properties of p-hydroxyacetophenone oxime-thiourea-trioxane terpolymer [11].

In this connection many co-worker have made attempt to improve the conducting property by changing the composition of monomers of conducting polymers supported on the surface of terpolymer matrix to improve the electrical properties [12-20].

MATERIALS AND METHODS

All chemicals used as of A.R. grade. Doubly distilled water was used in the present investigation.

Preparation of m-CMF-I and m-CMF-II

A mixture of m-cresol (0.05 M), melamine (0.05 M) and formaldehyde (0.15 M) with 1M HCl was refluxed over oil bath at $120-125^{\circ}$ C for 6 hrs with stirring. The solid product so obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with hot water, dried and powdered. The product was repeatedly washed with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove copolymer which might be present along with the terpolymer. It was dissolved in 1M NaOH and reprecipitated using 1:1 HCl solution. The product, finally, collected by filtration, washed with hot water, dried and kept in vacuum. The yield was found to be 70%.

Similarly other terpolymer Ligand such as m-CMF-II was synthesized by increasing the molar proportion of mcresol and formaldehyde by keeping that of melamine constant. The proportion of m-cresol, melamine and formaldehyde in m-CMF-II is 0.1:0.05:0.2 respectively. The yield was found to be 74%. The synthetic details are summarized in Table 1

Parameters/conditions	Specifications	
Terpolymeric ligand	m-CMF-I	m-CMF-II
m-Cresol	0.05 M	0.1M
Melamine	0.05 M	0.05M
Formaldehyde	0.15 M	0.2M
Catalyst, 1 M HCl	100 mL	100mL
Temperature, ⁰ C	120-125	120-125
Time, hrs	6	6
Yield	70%	74%

Table 1: Synthetic details of terpolymeric ligands

Measurement of electrical conductivity: The purified powdered sample was crushed with acetone. In order to get fine powder, it was sieved with the help of 300 mesh sieve. The resin sample was paletalized by applying pressure of 20 tones inch⁻² without using binder. The pallets so obtained were rubbed on sand paper to remove the impurity on the surface. The surface was cleaned with acetone. The surface of pallet was coated with thin film of graphite paste in order to make it conducting. The pallets were then kept in oven at 60^oC for 5 hrs. The continuity between surface was checked by multimeter. The electrical conductance of the material was measured by using voltage-divider method. In this method, the DC electric current of known voltage (50V) was supplied by SMPS power supply. A known resistance was joined in series with sample holder of pallet. A voltage (V₁) across this known resistance (R₁) and voltage across this resistance (V₁), the resistance offered by pallet of sample was calculated. With the help of resistance, thickness and radius of pallet, the specific conductivity was determined.

RESULTS AND DISCUSSION

Elemental analysis: The terpolymeric ligands were analyzed for carbon, hydrogen, nitrogen and oxygen content [21]. The elemental analysis was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh. The details of elemental analysis are incorporated in Table (2).

Terpolymeric Ligands	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%O Found (Calc.)	Empirical formula of repeat unit	Molecular weight of repeating unit
m-CMF-I	57.28 (57.35)	5.92 (5.88)	30.87 (30.89)	5.93 (5.88)	$C_{13}H_{16}N_6O$	272
m-CMF-II	63.41 (63.49)	5.92 (5.82)	22.26 (22.23)	8.51 (8.46)	$C_{20}H_{22}N_6O_2$	378

Table 2: Elemental Analysis of terpolymeric ligands



Figure 1: IR spectra of m-CMF-I and m-CMF-II ligands



(a)NMR spectra of m-CMF-I



(b)NMR spectra of m-CMF-II

Figure 2: NMR spectra of m-CMF-I and m-CMF-II ligands

FTIR and NMR data of terpolymeric ligands: The IR spectra (figure 1) of m-CMF-I and m-CMF-II terpolymeric ligands were carried out at Pharmacy Department, Mahatma Jyotiba Phule Campus, R. T. M. Nagpur University and NMR spectra (figure 2 a and b) of m-CMF-I and m-CMF-II ligands were carried out at Sophisticated Analytical Instrumental Facility(SAIF) Punjab University, Chandigarh. The IR and NMR data of m-CMF-I and m-CMF-II are shown in Table 3 and 4 respectively.

Table 3: IR and NMR spectra of m-CMF-I ligands

IR (Frequency in cm ⁻¹)	Nature of fragment assigned	NMR δ(ppm)	Nature of fragment assigned
3360-3500	Phenolic (Ar –OH)	2.5	$Ar-CH_2$ proton
2900(m) to 2800(m)	-NH—	4.0	Phenolic group (ArOH).
1600-1610	Aromatic skeletal ring	4.3-4.7	-N H —bridges
1495to 1480	-NH— bending	4.5	Ar—NH ₂ proton
1300-1320	C-N str. (Aromatic Amine)	6.35 to 6.45	-N H —bridges
1450-1460, 1290-1300and 750-780	Methylene (-CH ₂ -)bridges	6.0 to 7.2	Aromatic proton (Ar-H)

Table 4: IR and N	MR spectra of m-CMF	-II ligand [22-28]
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IR (Frequency in cm ⁻¹)	Nature of fragment assigned	NMR δ(ppm)	Nature of fragment assigned
3300-3500	Phenolic –OH group	2.3 to 2.5	Ar—CH ₃ proton
3200 to 3300	Ar-NH ₂	2.6	$Ar-CH_2$ proton
1400-1610	Aromatic skeletal ring	4.3-4.5	-N H —bridges
1455-1460	Methylene (-CH ₂) bridges	4.8	Phenolic group (OH).
1280-1295and 760-790	Ar-CH ₂ -Ar moiety	6.5 to 7.2	Aromatic proton (ArH)
1190-1210	-C—O Str.(phenol)	6.8	Ar-CH ₂ -Ar moiety
830-840	Tetrasubstituted benzene ring		

According to data obtain in physicochemical methods, the tentative structures of terpolymeric ligands were assigned as shown in figure 3(a and b).



Figure 3: Tentative Structure of m-CMF-I and m-CMF-II

Electrical Conductivity:

The resistance of terpolymeric ligands as a function of temperature was calculated by indirect method known as voltage divider method. In this method, a constant source of 50 V DC was supplied into circuit where in sample holder and known resistance were connected in series. The digital voltmeter was connected to record voltage (V_1) across known resistance (R_1) . The resistance of the pallet at a given temperature is given by

$$R_2 = \frac{R_1 (V_T - V_1)}{V_1}$$
.....1

Where, R_2 = Resistance offered by sample, R_1 = known resistance, V_T =Total voltage supplied in circuit, V_1 = voltage across known resistance.

Resistivity ρ was calculated using relation

$$\rho = \frac{R_2 A}{T} \dots 2$$

Where, ρ = Resistivity in Ω cm, A= Surface area of pallet and T = Thickness of pallet in cm.

The conductivity measurements were made over wide range of temperature. The electrical conductivity (σ) varies exponentially with absolute temperature accordingly to well known Wilson's equation,

$$\sigma = \sigma^0 \cdot \exp^{-E_a}/kT \dots 3$$

Where, σ =electrical conductivity at temperature T, σ^0 = Electrical conductivity at T $\rightarrow \infty$, E_a= Activation energy of electrical conductance and k = Boltzmann constant

The above equation (3) has been modified as [29].

$$\log \sigma = \log \sigma^0 + \left(-\frac{E_a}{2.303kT}\right)\dots4$$

The electrical conductivity of terpolymeric ligands is shown in figure 4.



Figure 4: Electrical conductivity of terpolymeric ligands

Plots of log σ versus 1/T found to be linear with negative slope [30]. It will be seen from the plots (figure 4 a and b) of terpolymeric ligands that there is a consistent increase in electrical conductivity as the temperature rises. These trend is a characteristics of semiconducting [31, 32].

The activation energy evaluated by above methods are shown in Table 5.

Table 5: Activation energy of terpolymeric Ligands

Terpolymeric Ligands	Temperature Range(K)	Activation energy (kJ mole ⁻¹)
m-CMF-I	323-453	11.31
m-CMF-II	423-578	10.37

CONCLUSION

From all above observation it is concluded that the activation energy values of terpolymeric ligands increase in the order m-CMF-I > m-CMF-II. The mentioned order of activation energy is attributed due to increase in number of aromatic nuclei in repeating unit support the fact as the number of π electrons increases the activation energy of conduction decreases thereby supporting the structures of terpolymeric ligands. The electrical conductivity of ligands increases with increase in temperature (figure 4a and b). Hence the terpolymeric ligand shows semiconducting behaviour. The plots of log σ Vs 1/T is found to be linear which indicate that Wilson's exponential law $\sigma = \sigma_0^{(\Delta Ea/kT)}$ is obeyed.

Acknowledgement

Authors are grateful to Dr. M. T. Bharambe, Director, Institute of Science, Nagpur and Dr. R. H. Limsay, Head, department of chemistry for providing available facilities.

REFERENCES

[1] R N Singru, Der Pharma Chemica, 2011,3, 5, 123.

[2] P K Rahangdale, W B Gurnule, L J Paliwal and R B Kharat, *Synth. React.Inorg. Met. Org. Chem.*, **2003**, 33, 7, 187.

[3] G Yang, H G Zhu, B HLiang and X M Chen, J. Chem. Soc., Dalton Trans., 2001,580.

 $[4]\,M\,$ M Jadhav, L J Paliwal and N S Bhave , XIV, National Symposium and Workshop Vadodara, India Thermans. , **2004**, 250.

[5] Gautmann and O. L.E. Lyons, Org. Semiconductor. John Willey. New York, 1967.

[6] H P Singh and D Gupta . Ind.J. Pure & Appl. Physc., 1986, 24, 444.

[7] S S Ingle, V V Hiwase, A B Kalambe, Chem Sci. Trans., 2013, 2(1), 29.

[8] D T Masram, K P Kariya and N S Bhave, *E Polymers*, 2007, 75.

[9] W B Gurnule and D B Patle, *Der Pharmacia Lettre*, **2011**, 3, 6, 250.

[10] J S Dewar and A M Talati , J. Am. Chem. Soc., 1964, 86, 1592.

[11] M M Patel and R J Manavalan, *Macromol. Sci-Chem*, **1983**, 19 (A), 951.

[12] A D Kushwaha , V V Hiwase, A B Kalambe, S K Kapse , Arch. of Appl. Sci. Res., 2012, 4(3), 1502.

[13] S S Umare, A D Borkar, M C Gupta, Bull. Mater. Sci., 23(3), 2000, 235.

[14] E Matveena, R J Carracossa, M Palomino and Parkhutik, J. Appl. Polym. Sci. 2004, 94, 1752.

[15] A E Job, P S Hermann, D O Vaz and Mattoso, J Appl. Polym. Sci., 2001, 79, 1220.

[16] S K Kapse, V V Hiwase, A B Kalambe, J. Pharm and Chem Res., 2012, 4(3) 1734.

[17] R H Gupta, A B Zade, W B Gurnule, J. Appl. Polym. Sci., 2008, 109, 5, 3315.

[18] A N Gupta, V V Hiwase, A B Kalambe, J. Pharm and Chem Res., 2012, 4(5), 2475.

[19] A D Kushwaha, V V Hiwase and A B Kalambe, Der Pharma Chemica., 2012, 4,1, 557.

[20] S K Kapse, V V Hiwase and A B Kalambe, J Chem Pharm Res., 2012, 4,3, 1734.

[21] A D Kushwaha, V V Hiwase, A B Kalambe, Der Pharma Chemica, 2012, 4(1), 557. .

[22] J R Dyer, Application of Absorption Spectroscopy of Organic Compounds, 2nd Ed., New Delhi, 1972, 33.

[23] R M Silverstein and F X Webster, Spect. Identification of Org. Compd. 6th Edn. John Willey New York, 1998, 144.

[24] R M Silverstein, G C Bassler, Spectrometric Identification of Organic Compounds, 2nd Edn. John Wiley and Sons Inc., New York, **1967**, 80.

[25] I J Ballamy, The IR Spectroscopy of Complex Molecules; John Wiley and Sons. Inc., 1958, 142.

[26] R T Morrison and R N Boyd, Org. Chem. 6th Edn. Prentice Hall India Pvt. Ltd. 2004, 710.

[27] L D Field, S Sternell and J R Kalman, Org. Struct from spectra, John Willey and Sons, New York, 2nd Edn., **1969**, 29.

[28] P S Kalsi, Spectroscopy of Organic Compounds 6th Edn. New Age International Publishers, 2004, 9.

[29] I E Katon, Org semiconducting Polym. Marcel Decker, Inc. New York, 1968.

[30] A B Devate and D K Kulkarni, Ind. J. Appl. Physc., 1978, 16, 697.

[31] D TMasram, E-J Chem., 2009, 6, 3, 830.

[32] L Pardeshi , A Rasheed and R A Bhobe , J. Ind. Chem. Soc., 1999, 57,388.