Electrical conductance and thermokinetic parameters of newly synthesized terpolymeric ligands

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ABSTRACT
Terpolymeric ligand (m-CMF-II) was synthesized by acid catalysed polycondensation of m-cresol (0.1 M), melamine (0.05 M) and formaldehyde (0.2 M) at 120-125°C. Tentative structure of ligand was determined by physicochemical methods such as elemental analysis, IR and NMR. Activation energy of electrical conduction was determined by voltage divider method. Ligand was found to obey Wilson’s law. Thermokinetic parameters of thermal degradation were determined by Freeman-Carroll (FC) and Sharp-Wentworth (SW) method. Thermokinetic parameters such as activation energy ($E_a$), apparent entropy ($\Delta S$), free energy ($\Delta G$) determine by both methods were in good agreement. Degradation was found to be first order.

Keywords: Terpolymer, TGA, Polycondensation, Electrical conductivity

INTRODUCTION

Formaldehyde based terpolymeric resin have great importance and advantage over copolymer due to high heat resistivity, thermal stability and low conduction activation energy. Last two decades have been seen an ever increasing interest in electrical properties of polymer which have industrial uses owing to low production cost and ease of manufacture [1]. One of the fundamental challenges therefore is to design thermally stable such conducting polymers with low band gap that there is no need to dope them [2]. In fact conductivity depends upon the external condition such as temperature, humidity, pressure, thickness of sample as well as its chemical structure [3, 4]. Thermally stable conducting polymer recently became boon to polymer chemist due to applicability at elevated temperature beside challenges that have to face owing to thermal instability and low processability.

In this connection many co-workers have made an attempt to improve the thermal stability and conducting property by changing the composition of monomers and by deposition of conducting polymers on the surface of terpolymer to satisfy electrical properties [5-13].

EXPERIMENTAL SECTION

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

Preparation of m-CMF-II
A mixture of m-cresol (0.1 M), melamine (0.05 M) and formaldehyde (0.2 M) with 1M HCl was refluxed over oil bath at 120-125°C for 6 hrs with stirring [14]. 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%.

**Measurement of electrical conductivity**

The purified powder 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 15 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°C for 5 hrs. The continuity between surfaces 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 circuit in series with sample holder of pallet. A voltage ($V_1$) across this known resistance ($R_1$) was recorded as a function of temperature. With the help of total voltage supplied ($V_T$), known resistance ($R_1$) and voltage across this resistance ($V_1$), 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:** Terpolymeric ligand was analyzed for carbon, hydrogen, nitrogen and oxygen content. The elemental analysis was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh. Details of elemental analysis are incorporated in Table 1.

<table>
<thead>
<tr>
<th>%C (Found)</th>
<th>%H (Found)</th>
<th>%N (Found)</th>
<th>%O (Found)</th>
<th>Empirical formula of repeat unit</th>
<th>Molecular weight of repeating unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.41</td>
<td>5.92</td>
<td>22.26</td>
<td>8.51</td>
<td>C$<em>{20}$H$</em>{22}$N$_6$O$_2$</td>
<td>378</td>
</tr>
</tbody>
</table>

**FTIR and NMR data of terpolymeric ligand:** IR spectra of m-CMF-II terpolymeric ligand was carried out at Pharmacy Department, Mahatma Jyotiba Phule Campus, R. T. M. Nagpur University and NMR spectra of m-CMF-II ligand was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh which is presented in Table 2.

<table>
<thead>
<tr>
<th>IR (Frequency in cm$^{-1}$)</th>
<th>Nature of fragment assigned</th>
<th>NMR $\delta$ (ppm)</th>
<th>Nature of fragment assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300-3500</td>
<td>Phenolic –OH group</td>
<td>2.3 to 2.5</td>
<td>Ar--CH$_3$ proton</td>
</tr>
<tr>
<td>3200 to 3300</td>
<td>Ar–NH$_2$</td>
<td>2.6</td>
<td>Ar--CH$_2$ proton</td>
</tr>
<tr>
<td>1400-1610</td>
<td>Aromatic skeletal ring</td>
<td>4.3- 4.5</td>
<td>–NH–bridges</td>
</tr>
<tr>
<td>1455-1460</td>
<td>Methylene (–CH$_2$) bridges</td>
<td>4.8</td>
<td>Phenolic group (–OH)</td>
</tr>
<tr>
<td>1280-1295 and 760-790</td>
<td>Ar–CH$_2$–Ar moiety</td>
<td>6.5 to 7.2</td>
<td>Aromatic proton (Ar–H)</td>
</tr>
<tr>
<td>1190-1210</td>
<td>–C–O (Aromatic Ring)</td>
<td>6.8</td>
<td>Ar–CH$_2$–Ar moiety</td>
</tr>
<tr>
<td>830-840</td>
<td>Tetrasubstituted benzene ring</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to data obtain in physicochemical methods; the tentative structure of terpolymeric resin was assigned as shown in Figure 1.

**Electrical Conductivity:** Resistance of terpolymeric ligand 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 given to the sample holder in series with known resistance (1M$\Omega$) across which digital voltmeter was connected to record voltage with increase in temperature. Resistance of the pallet at a given temperature is given by:
\[
R_2 = \frac{R_1 (V_T - V_2)}{V_f}
\]

Where, \(R_1\) = Resistance of pallet, \(R_2\) = known resistance (1MΩ), \(V_T\) = Total voltage supplied and \(V_2\) = Voltage across known resistance. Resistivity \(\rho\) was calculated using relation:

\[
\rho = \frac{R_2 A}{T}
\]

Where, \(\rho\) = Resistivity in Ω cm, \(A\) = Surface area of pallet and \(T\) = Thickness of pallet.

Conductivity measurements were made over wide range of temperature. Electrical conductivity \((\sigma)\) varies exponentially with absolute temperature accordingly to well known Wilson’s equation:

\[
\sigma = \sigma^0 \exp \left(-\frac{E_a}{kT}\right)
\]

Where, \(\sigma\) = electrical conductivity at temperature \(T\), \(\sigma^0\) = Electrical conductivity at \(T\rightarrow\infty\), \(E_a\) = Activation energy of electrical conductance and \(k\) = Boltzmann constant.

Above equation (3) has been modified as [22]:

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

According to above equation, a plot of \(\log\sigma\) vs. \(1/T\) would be linear with a negative slope as shown in Figure 2. In present study activation energy of terpolymeric ligand was found to be 10.37 kJ mole\(^{-1}\). Terpolymer shows electrical conductivity in the range of 0.59 x 10\(^{-7}\) mho cm\(^{-1}\) to 2.19 x 10\(^{-7}\) mho cm\(^{-1}\). Examination of data reveals that electrical conductivity increase in temperature hence terpolymer shows semiconducting behaviour in temperature range 155-305°C [23-25].

![Figure 2: Electrical conductivity of m-CMF-II resin](image)

**Thermogravimetric analysis:** The thermogram of m-CMF-II terpolymeric ligand as shown in Figure 3 was recorded at Dept. of Material Science, VNIT Nagpur using Perkin Elmer Diamond TGA/DTA analyzer in argon environment. The polymeric sample was allowed to heat upto 1110°C. The thermogram reveals that initial weight
loss up to 150°C due to loss of water. FC and SW plots are shown in Figure 4a, 4b. The order of decomposition was found to be 1.0 for m-CMF-II as determined by FC methods which were confirmed by SW method.

![Figure 3: Thermogram of m-CMF-II](image)

The thermokinetic parameters evaluated by above methods are shown in Table 3.

The thermokinetic parameters were determined by using following methods.

A) **Freeman-Carroll Method (FC):** In this method, kinetic parameters determined by following expression [26-27].

\[
\Delta \log\left(\frac{dw}{dt}\right) = \left[ -\frac{E_a}{2.303 R} \right] \times \Delta \left(\frac{1}{T}\right) + n
\]

Where; \(\frac{dw}{dt}\) = Rate of change of weight with time, \(W_r\) = difference between weight loss at completion of reaction and at time \(t\), \(E_a\) = activation energy, \(n\) = order of reaction

B) **Sharp-Wentworth method (SW):** Following expression is used to evaluate the kinetic parameters [28-31].

\[
\log \left(\frac{d\alpha}{dt}\right) = \log \frac{A}{\beta} - \frac{E_a}{2.303 RT}
\]

Where, \(d\alpha/dt\) = fraction of weight loss with time, \(n\) = the order of reaction, \(A\) = frequency factor, \(\beta\) = linear heating rate and \(\alpha\) = the fraction of amount of reactant.

<table>
<thead>
<tr>
<th>Thermokinetic parameters</th>
<th>m-CMF-II</th>
<th>FC method</th>
<th>SW method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a) (kJ)</td>
<td>39.99</td>
<td>39.51</td>
<td></td>
</tr>
<tr>
<td>Frequency Factor (min(^{-1}))</td>
<td>68.55</td>
<td>187.9</td>
<td></td>
</tr>
<tr>
<td>(\Delta S) (JK)</td>
<td>-244.03</td>
<td>-207.1</td>
<td></td>
</tr>
<tr>
<td>(\Delta G) (kJ)</td>
<td>184.43</td>
<td>162.11</td>
<td></td>
</tr>
<tr>
<td>Order (n)</td>
<td>1.01 ~ 1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FC= Freeman-Carroll  SW=Sharp-Wentworth
CONCLUSION

Elemental analysis and spectral studies such as IR and NMR data are in good agreement with assigned tentative structure of m-CMF-II terpolymer ligand. Electrical conductivity of ligand increases with increase in temperature which indicates its semiconducting behaviour in experimental temperature range of 428-578K. Semiconducting terpolymer may be used as transistors, integrated circuits (IC) for low cost as well as chemical sensors in electronic devices. Plots of log $\sigma$ vs. $1/T$ is found to be linear which indicate that Wilson’s exponential law $\sigma = \sigma_0 \exp^{-\Delta E_a/TK}$ is obeyed. Values of activation energies, apparent entropy and free energy of first order degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. Low value of frequency factor and entropy indicate the slow degradation. High value of energy of activation relative to thermal energy suggests that the m-CMF-II resin is thermally stable below 400°C.

Acknowledgement

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REFERENCES