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Original Article

Kinetic and Electrical Conductivity Study of Resin Resulting from Salicylic Acid and Phenylenediamine with Formaldehyde

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A B S T R A C T

The resin SPDF has been synthesized through condensation of salicylic acid and phenylenediamine with formaldehyde via hydrochloric acid as catalyst in the ratio 1:1:2. Comprehensive thermal degradation studies of this resin have been approved to establish its thermal stability. Electrical conductivity measurements have been also conceded out to learn the semiconducting nature of the resin.

The activation energy (Ea) calculated by with the Sharp-Wentworth method (15.03 kJ/mol) has been found to be in good agreement with that calculated by Freeman-Carroll (16.92 kJ/mol) method. A thermodynamic parameter such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S*) and frequency factor (Z) have also been evaluated on the basis of the statistics of Freeman–Carroll method. The order of reaction (n) is found out to be 0.98. The newly synthesized SPDF resin was found to be thermally stable and semiconducting in nature.

Keywords: Resin, Condensation, Thermal stability, Decomposition, Electrical conductivity.

INTRODUCTION

The advancement in the field resins has been awfully fast, as they normally obliging in packaging, adhesives and coatings in electrical sensors and organometallic semiconductors[1-4]. The reins tenders novelty and versatility; hence they have occupied the crucial site in the field of material science. A phenol group based resins have a large number of convenient applications in electronic controls, insulating materials, protective adhesives, aerospace industries, etc. because of their high thermal

stability, heat and chemical resistance and electrical insulation properties[5-12]. Semiconductors are the vital ingredients of contemporary electronics. The concerted research endeavors have been approved for mounting organic materials that would possesses superior electrical properties as the inorganic semiconductors. The prime attention was positioned on the synthesis of highly conductive polymers, preferably of high molecular weight and the measurement of their electronic conductivity properties, i.e. conductivity, mobility, thermo-electric power, etc. The resins have been identified for their recital as semiconductors while carrier mobility in them frequently is actuallittle[13-18]. Kand A *et al*[19,20] described the rubeanato-copper semi-conductive polymers and deliberate their AC and DC conductivity. Dhawan and coworkers[21] testified the conducting polymers forecast to be the revolutionary materials for the progress of light emitting diodes, antistatic and EMI materials, sensors, Opto-electronic devices and rechargeable batteries owing to their brilliant conduction mechanism and superior environmental consultancy. The Freeman–Carroll and Sharp-Wentworth methods have been pragmatic for the cunning of kinetic parameters[22-24]. Approaches for the assessment of kinetic parameters from thermogravimetric readings are customarily grounded on the supposition to the Arrhenius equation are substantial with thermal and diffusion barriers are insignificant. For the electrical conductivity measurement study the DC resistance of the SPDF resin had been measured by smearing a constant voltage (50 volts) across the pellets. The temperature reliance of the electrical conductivity of the resin is then plotted. The energy of activation (E_a) of electrical conduction calculated from the slopes of the plots. The electrical conductivity of the resin had been studied with a rise in temperature.

EXPERIMENTAL SECTION

Chemicals

All Chemicals had been applied are of AR grade. Salicylic acid, Phenylenediamine has been purchased from Aldrich Chemical Co., USA and Formaldehyde from LOBO Chem., India, DMF and DMSO (HPLC grade) were used.

Instruments used

Thermogravimetric analyses (TGA) of the resin sample had been approved by Perkins Elmer TGS-ll thermal analyzer at a heating rate of 10^0C per minute in air atmosphere upto 800^0C. The thermogram had been noted as Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujrat, India. The electrical resistivity of the resin had been designed by Hewlett-Packard 4192 Impedance analyzer 5Hz-13MHz at Department of Physics, RTM Nagpur University, Nagpur over a wide range of temperature of 313-423 K.

Synthesis and characterization of SPDF resin

A combination of salicylic acid, phenylenediamine and formaldehyde in the molar proportion 1:1:2 with hydrochloric acid as catalyst had been animated in an oil bath at 120^0C for 7 hours. The resinous product had been dehydrated in the air and crushed with mortar and pestle. The product had been extracted with diethyl ether and petroleum ether to eradicate salicylic acid-phenylenediamine and copolymers that might be present with the resin. It was further purified by dissolving in 8% sodium hydroxide solution, reprecipited by the steady drop wise addition of 1:1 (v/v) hydrochloric acid by normal stirring to shun lump formation[22-26]. The resin was filtered and purity checked with thin layer chromatography method. The resin is soluble in DMF, DMSO. However, it was insoluble

in acids and common organic solvents. Our manuscript[27] reveals the characterization of resin by elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and UV- Visible spectral studies. The number average molecular weight of the resin had been determined by non-aqueous conductometric titration.

The structure of newly synthesized resin has been specified underneath **(Fig -1).**

Thermogravimetry

Thermal analysis progression was correlated through a transform in weight with reverence to temperature. Heating was performed under firmly proscribed circumstances and could divulge changes in arrangement and other vital properties of the material being studied **(Table -1)**. In dynamic TGA the sample is subjected to circumstances augment in temperature at linear pace[28,29].

The benefit of Freeman and Carroll technique was that in a single step by keeping the heating rate steady the order of reaction and energy of activation could be calculated in a sole experiment. The subsequent equation had been applied to estimate diverse kinetic parameters **(Table -2)**:

$$\frac{\Delta \log dw/dt}{\Delta \log Wr} = n - \frac{Ea}{2.303R}.\frac{\Delta(1/T)}{\Delta \log Wr}$$

Consequently, a plot of $\frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta \log W_r}$ vs. $\frac{\Delta (1/T)}{\Delta \log W_r}$ should bid a straight line with an intercept on y-axis identical to the value of n (the order of reaction) and the slope m = E / 2.303R.

Where,

dw/dt= rate of change of weight with time and in expression Wr = Wc –w,

W_c= weight loss at the completion of the reaction, w is the total weight loss up to the time t and T is the temperature in k.

The following expression is used to evaluate Ea with Sharp- Wentworth method:

$$\log \frac{(dc/dT)}{(1-c)} = \log(A/\beta) - \left[\frac{E_a}{2.303R}\right].\frac{1}{T}$$

Where,

dc/dt = the rate of change of mass with time t, T is the temperature and β= ΔT/dt.

Electrical conductivity

The resins are recognized for their performance as semiconductors though carrier mobility in them is awfully low. This is owing to the complexity which electrons experience in jumping from one molecule to another. Thus the carrier mobility in compounds of these sort increases with the rise in molecular size[16-20,28-31].

Resin had been palatalized isostatically in a steel die at 10 tonnes/2inch with a hydraulic press. A thin layer of colloidal graphite which functions as electrode had been applied on both sides of the pellets in acetone and desiccated at room temperature for 6 hours. The average diameter of this pellet and its thickness were calculated with Screw Gauze. The temperature variations of resin were studied by placing the sample holder along with the pallet in the electric furnace that was then heated slowly. The slow rate of heating 1 to 10 ^{0}C per minute was maintained throughout the investigation. The resistances of the sample pallets were measured by two probes (terminals) method.

Resistivity (ρ) was then calculated using the relation: ρ = R. x A/l.

Where, R= resistance of the pellet; A = Surface area of pellets & l = Thickness of pellet.

The DC resistivities were measured from 313 to 423 K. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the well-known relationship.

$\sigma = \sigma_0 \exp^{-Ea/kT}$

Where,

σ=electrical conductivity (T); $\sigma_{0=}$ electrical conductivity; Ea =Activation energy of electrical conduction; K= Boltzmann constant; T= Absolute temperature.

The relationship has been modified as:

Log σ = logσ0 + -Ea/2.303kT.

Rendering to this equation, a plot of Log σ Vs 1/T would be linear with negative slope (Fig-3). From the Slope of the plots, the activation energy was calculated (Table -3).[12-16,28-31]

RESULTS AND DISCUSSION

Thermal degradation study for SPDF resin

Thermal degradation curve for SPDF resin was revealed in **Fig. 2** exhibits a four-stage decay and its ranges were given in **Table-1**.The first phase decay, which was unhurried and reached from 40-210^{o}C agreeing to lose 5.8% which may be due to entrapped H_2O fragment. The second step decay signifies deprivation of -OH and -COOH group. The pragmatic mass loss is 22.5%. The third stage putrefaction is due to the loss of adjacent shackle phenolic -OH group and observed 68.5%. The fourth state decomposition resembles to total breakdown of the resin. The Half Decomposition temperature of SPDF resin was originated to be 225^{o}C.

As per thermogram activation energy deduced with Freeman – Carroll and Sharp-Wentworth approaches were in fine accord with each other. Thermodynamic parameters had been calculated on the origin of thermal activation energy and standards were quantified in **Table 2**. Due to the abnormally little value of frequency factor [Z] it may be classified as a dawdling reaction. The assessment of entropy [ΔS] indicates the activated polymer had additional ordered assembly than the reactants. This was further braced by low Z values[22-25,28-32]. It was awfully complicated to depict any elite inference from the magnitude of thermal activation energy [Ea] as disintegration mechanism was expected to be complicated. Positive values of activation energy present examination connect the energy of activation due oxidation–reduction process of resin in the higher temperature range[22-24,28-32]. This was expected, since, the decomposition of the resin was not obeying first order kinetics perfectly. These clarifications are in accord with the assumption of Jacobs and Tompkin and other previous researchers[33].

Electrical conductivity of SPDF resin

The significances of electrical conductivity and activation energy were integrated in **Table 3**. The temperature dependence of the electrical conductivity of the resin was revealed in **Fig.3**. The electrical conduction of polymeric material depends upon inestimable parameters such as porosity, pressure, method of preparation, ambiance etc; activation energy (Ea) was not affected by these parameters and, therefore, it was rather reproducible[22,24,34-37]. The extent of activation energy depends on the number of electrons existing in semiconductor ingredients. The low degree of activation energy may owe to companies of more amounts of JI-electrons in the chain. This was in good promise with the most practicable organization anticipated for the newly blended resin under exploration[12-16]. The carrier motilities of the organic semiconductors might decrease due to:

- The forces between the adjacent molecules are comparatively weak as organic compounds from molecular crystals.
- Due to modest electronic coupling that exists among the contiguous molecules, it becomes difficult for the electrons to hop from one molecule to another.
- As an effect of the tangled configuration which is due to amorphous nature, the electrons get speckled while itinerant through the materials, when they attempt

to stream through it and hence lower the conductivity.

The study shows the following results of electrical conductivity-

- The electrical conductivity of the SPDF resin at room temperature lies in the range of 2.29 x10^{-11} to 2.36x10^{-7} Siemen.
- The plots of log (versus 1/T were found to be linear in the temperature range under study, which indicate that the Wilson's exponential law (= (o exp (ΔE/kT) is obeyed.
- The energy of activation (Ea) of electrical conduction calculated from the slopes of the plots was found to be in the range of 1.59 x 10^{-22} J/K.

These remarks and domino effect were in harmony with the conclusion of former workers[12-16,22,24,34-37]. Electrical conductivity of each of the resin increases to rise in temperature. Hence, the resin may be ranked as semiconductors.

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REFERENCES

1. Coppo P., Schroeder R., Grell M., Turner M.L.; Investigation of the electronic properties of cyclopenta-dithiophene polymers and copolymers Materials Research Society Symposium Proceedings 771 (Organic and Polymeric Materials and Devices), CODEN: *MRSPDH*; ISSN: 2003, 0272-9172, 61-64.
2. Kang S.W., Kim J.H., Oh K.S., Won J.; Effect of amino acids in polymer/silver salt complex membranes on facilitated olefin transport. *J. of Membrane Sc*., 2004; 248: 201–206.
3. Nezel T., Fakler A., Zhylyak G., Mohr G.J., Keller S.; A highly sensitive NO_2-selective optode membrane, *Sensors and Actuators B*, 2000;70:165–169.
4. Coppo P., Grell M., Turner M.L.; Cyclopentadithiophene based electro-active materials; *J. Mater. Chem*., 2005, 15: 1123–1133.
5. Colin F. P., Rena M. P.; Thermally stable, highly fluorinated stationary phases for gas chromatography, *Analytica Chimica Acta*; 1987; 200:151-169.
6. Chandra R., Rajabi L., Soni R. K.; The effect of bismaleimide resin on curing kinetics of epoxy-amine thermosets, *J. of Appl. Polym. Sc*.; 1996; 62, 4:661-671.
7. Masram D.T.; Thermal Degradation Study of Terpolymer Resin derived from Salicylic acid, Diaminonaphthalein, Formaldehyde Terpolymer, E- *J. of Chemistry*; 2009; 6(3):830-834.
8. Das A.P.; S. Lenka; Nayak P.L.; Synthetic resins: I. Preparation and characterization of resins from substituted benzoic acid-formaldehyde, *J. Appl. Polym. Sci*. 1985; 30:4619.
9. Aristove L.J.; Kostantinov V.V.; Polymers with chelate bonding, derived from 8-quinolinol.; Izu. *Tomsk. Politekhn. Inst*.; 1961; 111: 104-6.
10. Samal R.K., Senapati B.K., Behuray T.B.; Synthesis and Characterization of Aniline-Doped Mixed Copolymer Resins-2., *J. Appl. Polym. Sci*.; 1996; 62 :655.
11. DeGeiso R.C.; Donaruma L.G.; Tomic, E A., Polymeric Ligands, Separation of Uranium from Solutions and Ore Leaches with Salicylic Acid-Formaldehyde Polymers, *Ind. Eng. Chem. Process Des. Dev., ACSpub*.; 1963; 2 (1):43–44.
12. Masram D.T., Kariya K.P., Bhave N.S.; Thermal degradation and electrical conductivity measurement study of resin

derived from salicylic acid, hexa-methylenediamine and formaldehyde" *Elixir Appl. Chem*. 2012, 48, 9557-9562., ISSN 2229-712X.
13. Masram D.T., Kariya K.P., Bhave N.S.; Kinetics of Thermal Degradation Study of Resin derived from Salicylaldehyde, Ethylenediamine and Formaldehyde; E-*J. of Chemistry*; 2010;7(2), 564- 568.
14. Ozawa T.; Applicability of Friedman Plot; *J. Thermal Analysis*; 1986; 3l: 547-551.
15. Manvalan R.; Patel M.M.; Synthesis and Study of Tercopolymers; *J. Macromolecular Chem*.; 1983; A-20 (9): 907-925.
16. TalatiA. M and Mistry V.N.; Semiconducting chelate polymers of dihydroxyquinones with cobalt Polymères semi-conducteurs de chélate par les dihydroxy-quinones avec le cobalt Halbleitende spheron polymer von dihydroxy-chinonenmitkobalt. *Materials Sc. and Eng*.; 1972; 10: 287-290.
17. Han G., Shi G.; Porous polypyrrole/ poly methyl methacrylate composite film prepared by vapor deposition polymerization of pyrrole and its application for ammonia detection. *Thin Solid Films*; 2007; 515, 17: 6986-699.
18. Kharadi G.J.; Panchani S.C.; Patel K.; D. Studies on Some Coordination Polymeric Chains of Metal Ions with QM1N. *International Journal of Polymeric Materials*; 2010; 59, 8, 577 - 587.
19. Kanda S., Kawaguchi S.; Electrical conductivity of some coordination polymers. *J. Chem. Physics*; 1961; 34; 1070.
20. Kanda S. , Kawaguchi S.; Synthesis of Co-ordination Compounds of High Molecular Weight. *Bulletin of the Chemical Society of Japan*; 1957; 30, 2: 192-193.
21. Dhawan S.,Koul S., Chanda S.; *National Seminar on Polymer*, Chennai, 24, 1996.
22. Masram D.T., Kariya K.P., Bhave N.S.; Kinetic and Electrical Conductivity Measurement Study of SDBF Resin" *International Journal of Engineering Research*, 2013, 2, 2, 165-170, 01, ISSN: 2319-6890.
23. Masram D.T., Kariya K.P., Bhave N.S.; Synthesis, characterization and thermal degradation study of terpolymer derived from p-hydroxybenzoic acid, diaminonaphthalene with formaldehyde, *High Perform. Polym*.; 2010; 22, 8:1004 -1016.
24. Masram D.T., Kariya K.P., Bhave N.S.; Thermal degradation and electrical conductivity measurement study of resin derived from salicylic acid, hexa-methylenediamine and formaldehyde" *Elixir Appl. Chem*. 2012, 48, 9557-9562., ISSN 2229-712X.
25. Jadhao M.M., Paliwal L.J., Bhave N. S.; Resin I: Synthesis and characterization of 2, 2′-dihydroxybiphenyl-urea-formaldehyde terpolymers, *J. Appl. Polym. Sci*.; 2005, 96, 5; 1605 - 1610.
26. Masram D.T., Kariya K.P., Bhave N.S.; Synthesis of Resin-I: Salicylic acid hexamethylenediamine and Formal-dehyde and its ion exchange properties, *Epolymers*; 2007; ISSN 1618-7229, 75.
27. Masram D.T., Kariya K.P., Bhave N.S.; Analytical Applications of Newly Synthesized Resin Derived From Salicylic Acid, Phenylenediamine And Formaldehyde" *Der Pharma Chemica*, Scholars Research Library, 2012, 4, (3): 1239-1246 ISSN 0975-413X.
28. Freeman E.S., Carroll B.J.; The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate,; *Phys. Chem*. 1958, 62, 4, : 394–397.

29. Freeman E.S., Anderson D.A.; The kinetics of the thermal degradation of polystyrene and polyethylene, *J. Polym*.; 1961; 54, 159:253 – 260.
30. Sharp J.B.; Wentworth S.A.; Kinetic analysis of thermogravimetric, *Anal. Chem*. 1969; 41 (14): 2060–2062.
31. Coats A.W.; Redfen J.P.; Kinetic parameters from thermogravimetric data. II; *J. of Polym. Sc. Part B: Polymer Letters*, 2003**,** 3, 11:917 – 920.
32. Ozawa T.; Kinetics of non-isothermal crystallization; *J. Thermal Analysis*; 1971, 12, 3: 150-158.
33. Jacobs P.W.M.; Tompkins F.C.; *Chemistry of Solids State, E.G., Garner Publication, London;* 1955, 188.
34. Azaroff L.V.; *Introduction to Solids, McGraw Hill Inc. New york*; 1960.
35. Dunlop W.V.; *An introduction to semiconductors, Wiley, New York*,; 1957, 189.
36. Fanun M.; Conductivity, viscosity, NMR and diclofenac solubilization capacity studies of mixed nonionic surfactants microemulsions. *J. Molecular Liquids*; 2007, 135, 1-3:5-13.
37. Masram D.T., Kariya K.P., Bhave N.S.; "Electrical conductivity study of resin synthesized from salicylic acid, butylenediamine and formaldehyde," *Archives of Applied Science Research*; 2010, 2(2):153-161.

Table 1. Thermo analytical facts and decomposition temperature of SPDF

Resin	Temperature range (°C)	Stage of decomposition	Species degraded	% Weight loss	
				Observed	Calculated
SPDF	40-210	First	Loss of entrapped - H_2Omolecule	5.8	6.2
	210-320	Second	Loss of -COOH and -OH group	22.5	23.6
	320-580	Third	Loss of side chain attached to aromatic nucleus	68.5	68.8
	580-800	Fourth	Complete decomposition	100	100

Table 2. Kinetic parameters of SPDF

Resin	Decomposition Temp. (T)	Half Decomposition Temp. (T*)	Activation Energy kJ/mole		Kinetic parameters by FC				
			FC	SW	ΔS (J)	ΔF (kJ)	z (S^{-1})	S*(J)	n
SPDF	274	478	16.92	15.03	8.19	13.0	902.81	-22.8803	0.98

FC= Freeman – Carroll Method: SW= Sharp-Wentworth Method: n= order of reaction: Temp. = Temperature

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Table 3. Evaluation of activation energy of conduction

Temp (K)	1000/T (K^{-1})	Resistance in Ohm 'R'	Resistivity p = RA/l (Ohm.cm)	Electrical Conductivity σ = 1/ρ (Siemen.cm^{-1})	Logσ
313	0.0032	9.76×10^{9}	6.02×10^{10}	1.66×10^{-11}	-10.7799
318	0.0031	7.25×10^{9}	4.47×10^{10}	2.23×10^{-11}	-10.6508
323	0.0031	5.98×10^{9}	3.69×10^{10}	2.71×10^{-11}	-10.5671
328	0.0030	3.78×10^{9}	2.33×10^{10}	4.29×10^{-11}	-10.3679
333	0.0030	1.31×10^{9}	8.09×10^{9}	1.24×10^{-10}	-9.9077
338	0.0030	8.63×10^{8}	5.33×10^{9}	1.88×10^{-10}	-9.7265
343	0.0029	5.97×10^{8}	3.68×10^{9}	2.71×10^{-10}	-9.5664
348	0.0029	3.17×10^{8}	1.96×10^{9}	5.11×10^{-10}	-9.2915
353	0.0028	1.02×10^{8}	6.30×10^{8}	1.59×10^{-9}	-8.7990
358	0.0028	8.98×10^{7}	5.54×10^{8}	1.80×10^{-9}	-8.7437
363	0.0028	7.23×10^{7}	4.46×10^{8}	2.24×10^{-9}	-8.6496
368	0.0027	6.41×10^{7}	3.96×10^{8}	2.53×10^{-9}	-8.5973
373	0.0027	5.19×10^{7}	3.20×10^{8}	3.12×10^{-9}	-8.5056
378	0.0026	3.86×10^{7}	2.38×10^{8}	4.20×10^{-9}	-8.3770
383	0.0026	2.23×10^{7}	1.38×10^{8}	7.27×10^{-9}	-8.1387
388	0.0026	1.13×10^{7}	6.97×10^{7}	1.43×10^{-8}	-7.8435
393	0.0025	9.74×10^{6}	6.01×10^{7}	1.66×10^{-8}	-7.7790
398	0.0025	7.99×10^{6}	4.93×10^{7}	2.03×10^{-8}	-7.6930
403	0.0025	4.12×10^{6}	2.54×10^{7}	3.93×10^{-8}	-7.4053
408	0.0025	3.08×10^{6}	1.90×10^{7}	5.26×10^{-8}	-7.2790
413	0.0024	2.14×10^{6}	1.32×10^{7}	7.57×10^{-8}	-7.1209
418	0.0024	1.02×10^{6}	6.30×10^{6}	1.59×10^{-7}	-6.7990
423	0.0024	9.82×10^{5}	6.06×10^{6}	1.65×10^{-7}	-6.7826

Diameter of the pellet = 1.282; Surface area of the pellet (A) = $\pi r^2 = 3.142 \times (0.641)^2 = 1.290$ cm^2; Thickness of pellet (l) = 0.209 cm;A/l = 6.176 cm.

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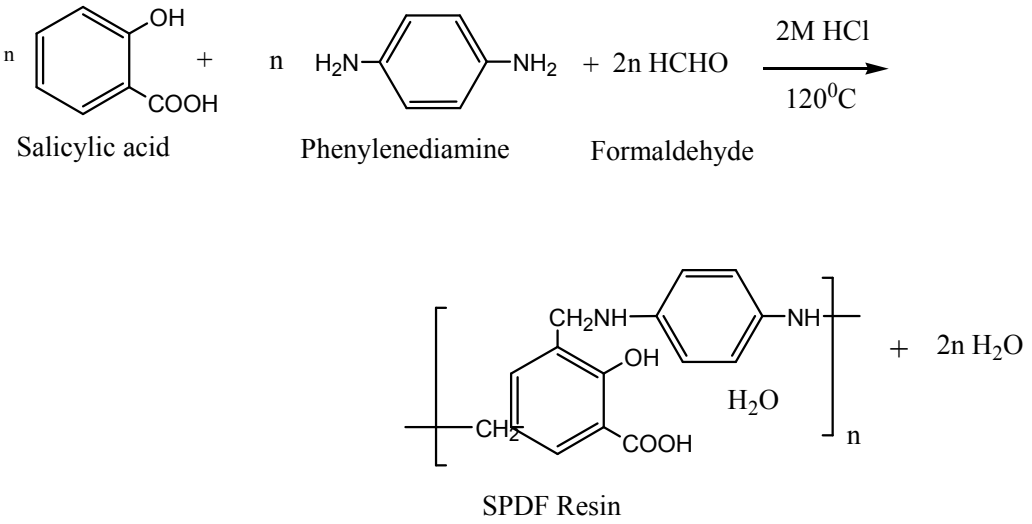

Figure 1. Synthesis of SPDF

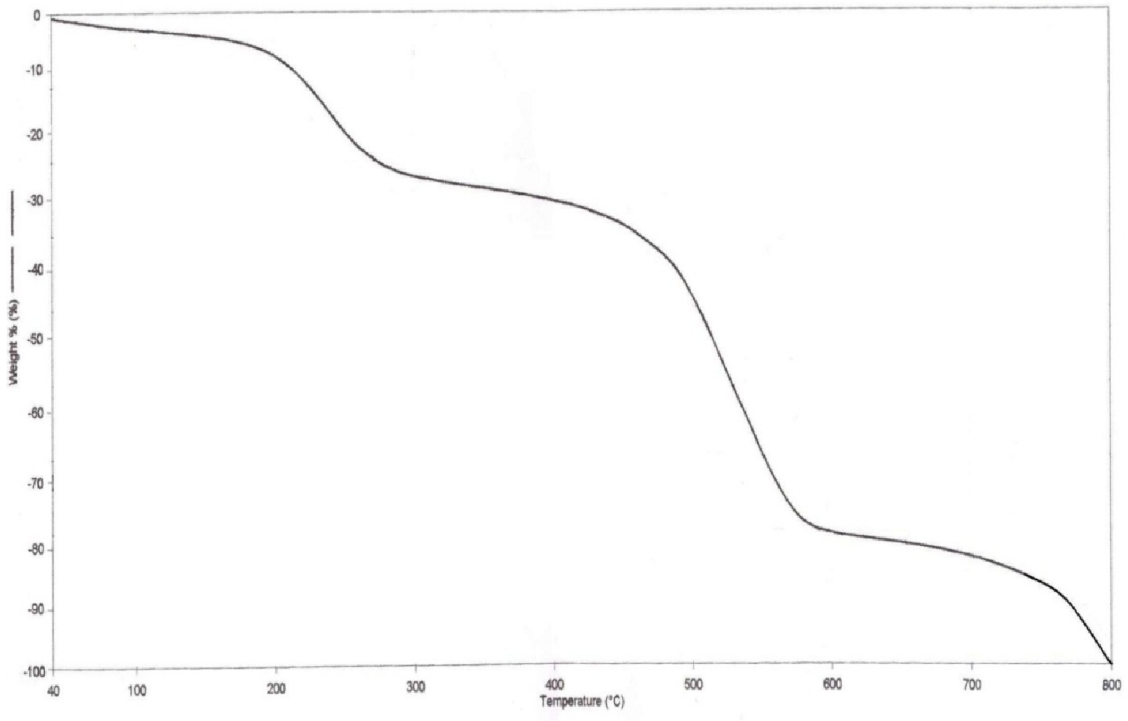

Figure 2. TGA curve of SPDF

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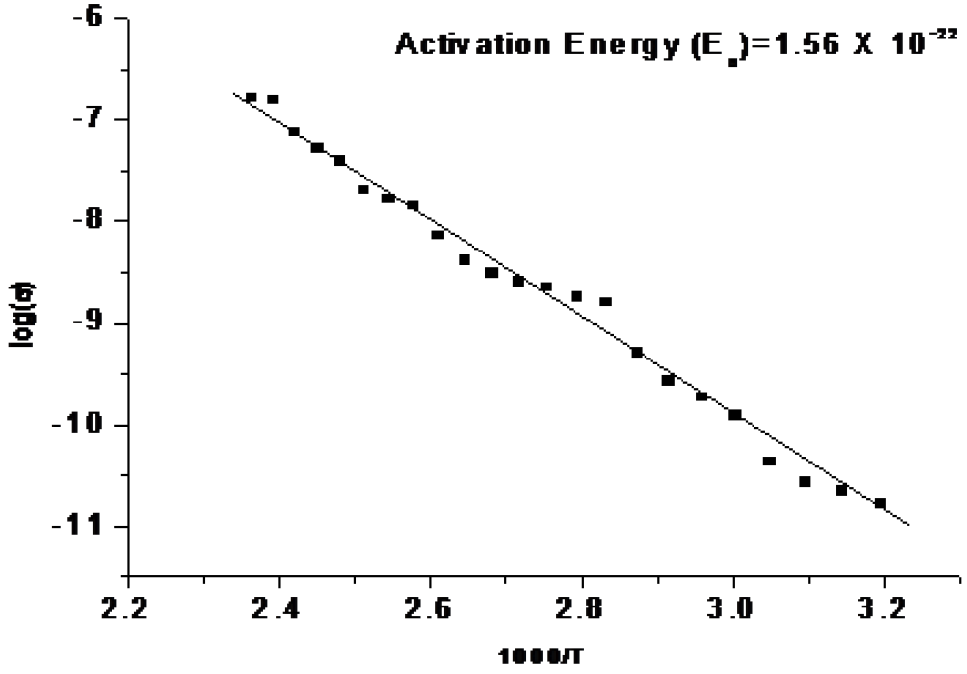

Figure 3. Electrical conductivity plots of SPDF