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Thermal Degradation Analysis of Melamine-Aniline-Formaldehyde Terpolymeric Ligand

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Abstract

Terpolymeric ligand MAF has been synthesized by the condensation of melamine (M) and aniline (A) with formaldehyde (F) in the presence of an acid catalyst in 1:2:4 molar proportions of the reacting monomers. The characterization of terpolymeric ligand has been done on basis of elemental analysis, IR and ^{1}HNMR. Thermal decomposition curve shows single decomposition step (305-530 ^{0}C). Thermal activation energy (E_a) calculated by Sharp-Wentworth (21.10 KJ/mole) method and Freeman-Carroll (21.46 KJ/mole) method are in good agreement. Freeman - Carroll and Sharp -Wentworth methods have been applied for the calculation of kinetic parameters while the data from the Freeman - Carroll methods have been used to determine various thermodynamic parameters.

Keywords: Terpolymeric ligand, Decomposition, Sharp-Wentworth method, Freeman-Carroll method, Thermodynamic parameters.

Introduction

Considerable amount of work has been reported on various copolymers, synthesized by the condensation of a mixture of phenol or various amines, and formaldehyde[1]. These resins have a large number of practical 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[2,3]. Various researchers have studied the applications of terpolymeric ligand of substituted phenols and formaldehyde[4].

By and large the studies of the thermal degradation of copolymer resins have become a subject of interest. Thermo-gravimetric study of 8-hydroxyquinoline-melamine-formaldehyde resin has also been carried out[5]. Terpolymer resins based on substituted *p*-cresol and melamine with formaldehyde have been synthesized and studied for its thermal properties[6].

The present communication deals with synthetic and thermal degradation properties of a newly synthesized terpolymeric ligand derived from melamine (M) and aniline (A) with formaldehyde (F). The elemental analysis has been carried out to ascertain the molecular formula and spectral analysis has been used to characterize the MAF terpolymeric ligand. The Freeman – Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters[7,8]. Methods for the estimation of kinetic parameters from thermo-gravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible.

Material and Methods

All the chemicals used were of analytical reagent grade. DMF was used after distillation.

Synthesis of Polymeric ligand: For synthesis of terpolymeric ligand[9,10] a mixture of melamine (0.05 mole), aniline (0.1 mole), formaldehyde (0.2 mole) in 200 ml HCl (2M) was refluxed on oil bath for 6 hours with occasional shaking. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was then purified by dissolving in (1M) sodium hydroxide solution, filtered and re-precipitated by gradual drop wise addition of ice cold (2M) HCl with constant and rapid stirring to avoid lump formation. The MAF terpolymeric ligand so obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel. The sample and amount of reactant of MAF terpolymeric ligand is given in table-1.

The estimation of carbon, hydrogen and nitrogen was done by the elemental analyzers Elementar Vario EL III Carlo Erba 1108 from C.D.R.I., Lucknow (India). Infrared spectra of the ligand was scanned at SAIF Chandigarh (India), in KBr pellet on Perkin Elmer, RX I in range 4000-500 cm^{-1}. NMR spectra were recorded on 60 MHz for one hour using BRUKER AVANCE II 400 NMR spectrometer at SAIF, Chandigarh (India). The spectra were recorded in (DMSO) d_6 solvent.

Thermal analysis: Thermal analysis method is associated with a change in weight with respect to temperature. Heating is

performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. In non-isothermal or dynamic TGA, the sample is subjected to condition where temperature is increased at linear rate.

Thermo-gravimetric analysis (TGA) of polymer sample was carried out by using Perkins Elmer Diamond thermal analyzer at heating rate of 10 ^{0}C per minute and in air atmosphere up to 1000^{0}C. The thermograms were recorded at Visvesvaraya National Institute of Technology, (VNIT) Nagpur (India).

The Freeman - Carroll and Sharp - Wentworth methods have been employed for the calculation of kinetic parameters of the newly synthesized terpolymeric ligand with help of dynamic TG curve[11,12].

The advantage of Freeman - Carroll method is that by keeping heating rate constant, both the order of reaction and energy of activation can be calculated in a single experiment. The following expression is used to evaluate various kinetic parameters[13,14] like activation energy (Ea), entropy change (ΔS), free energy change (ΔF), frequency factor (Z), apparent entropy change (S*) and the order of reaction (n) of the terpolymeric ligands and polychelates

Hence, a plot of log[dC_w / dt] / log W_r Vs [1/T] / log W_r should give a straight line with an intercept on *y*-axis equal to the value of n (order of reaction) and the slope m = Ea / 2.303R. Where, dCw/dt is the rate of change of weight with time and in expression Wr = Wc –W, Wc is the weight loss at the completion of the reaction, w is the total weight loss up to the time t and T is the temperature. The following expression is used to evaluate Ea with Sharp- Wentworth method

$$\frac{\log \dfrac{dC_w}{dt}}{\log W_r} = \frac{Ea}{2.303R}.\frac{\dfrac{1}{T}}{\log W_r} + n$$

$$\log\left[\frac{dC_w/dt}{1 \quad C_w}\right] = \log(A/\beta) \quad \left[\frac{Ea}{2.303\,R}\right].\frac{1}{T}$$

Where, dC_w / dt is the rate of change of mass with time t, T is the temperature and β = dT/dt

Results and Discussion

The newly prepared terpolymeric ligand was found to be yellow coloured solid soluble in dimethylformamide and dimethylsulphonoxide.

Characterization of terpolymeric ligand: The composition of terpolymeric ligand obtained on basis of elemental analysis data as shown in table-2 was found to be in good correlation to that of calculated values.

A sharp band appearing in the region 3350 cm^{-1} may be due to the stretching vibration of -NH- group[15,16]. The inflections around 1440.5cm^{-1}, 1265.0 cm^{-1} and 750.7 cm^{-1} suggest the presence of bending, wagging, rocking vibrations of methylene (-CH_2-) bridges in polymeric chains[17,18]. The sharp peak at 1610 cm^{-1} may be due to aromatic skeletal ring. The band presence at 1460 cm^{-1} may be due to symmetric tri-substituted melamine ring[16,17,19]. The broad bands at 1485.0 cm^{-1}, 770.4 cm^{-1} suggest the presence of -NH-bending, wagging in terpolymeric ligand respectively[17,20]. The IR spectral data of MAF terpolymeric ligand is summarized in table-3.

The NMR spectrum of the MAF terpolymer exhibit signal in the region of 6.34-7.36 δ (ppm), which may be due to the protons of the aromatic rings (Ar-H)[21,22]. The presence of a broad signal around 6.32 δ (ppm) is due to -NH- attached to melamine ring which is mixed with NH- of aromatic ring[19] . The presence of a broad signal around 6.89 δ (ppm) is attributed to the presence of –NH bridges[20,22]. A methylene protons Ar-CH_2- Ar appear as a singlet at 3.55 δ (ppm)[23]. The spectral data is tabulated in table-4.

Table-1
Sample and amount of reactants of $[MAF]_n$ terpolymeric ligand

Reactants (in moles)			Catalyst 2M HCl (aq.) (ml)	Reflux temp. ± 2^0 C	Terpolymeric ligand Abbreviation	Molar ratio of reactant	Yield (%)	M.P. (K)
M*	A*	F*						
0.05	0.1	0.2	200	102	$[MAF]_n$	1:2:4	75	578

* M = Melamine A = Aniline F = Formaldehyde

Table-2
Analytical Data of $[MAF]_n$ terpolymeric ligand

Terpolymer	Empirical Formula	%C		%H		%N	
		Found	Cal.	Found	Cal.	Found	Cal.
$[MAF]_n$	$C_{19}H_{22}N_8$	62.81	62.98	6.06	6.08	30.85	30.94

Table-3
IR Spectral data of $[MAF]_n$ terpolymeric ligand

Assignments	Observed band Frequency (cm^{-1})	Expected band Frequency (cm^{-1})
>NH stretch	3350	3500-3200
Methylene bridge (-CH_2) mode	1265 (w) 1440.5 (b) 750.7 (r)	1300-1200 1460 775
Tri -substituted melamine ring	1460	~1470
N-H wagging	770.4	650-800
N-H bending	1485	1400-1500

Table-4
^{1}H-NMR spectral data of $[MAF]_n$ terpolymeric ligand

Nature of proton	Chemical Shift δ (ppm)	Expected Chemical Shift δ (ppm)
Aromatic (Ar-**H**)	6.34-7.36	6.2-8.5
-NH- melamine	6.32	6.2-6.8
Ar – C**H$_2$ -N**	2.7	2.5-3
-N**H** bridging	6.89	5.4-8.5
Ar-C**H$_2$**- Ar	3.55	2.7-4.3

Table-5
Activation energy and decomposition temperature of $[MAF]_n$ terpolymeric ligand

Terpolymeric Ligand	Decomposition temperature (^oC)	Activation Energy (kJ/mol)	
		FC	SW
$[MAF]_n$	390	21.46	21.10

FC – Freeman-Carroll, SW – Sharp –Wentworth

Thermo-gravimetric studies of MAF ligand: Thermo-gravimetric analysis[24] of MAF ligand has been carried out and thermogram and kinetic plots for MAF terpolymeric ligand are given in figure-1, figure-2 and figure-3. The thermogram exhibits single decomposition step (305-530 °C). MAF terpolymeric ligand is stable up to 305°C. Up to 530°C gradual mass loss is observed because of the decomposition of polymer and beyond 530°C no mass loss takes place. This shows the formation of a stable species. The decomposition temperature for MAF terpolymeric ligand is 390°C. (Total mass loss: Calc. 79.34%, Obs. 78.00%).

Thermogram of MAF Terpolymeric ligand shows activation energy calculated by the Freeman - Carroll and Sharp - Wentworth methods are in good agreement with each other as given in table-5.

Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in table-6. Due low value of frequency factor [Z] it may be classified as a slow reaction. The negative value of entropy [ΔS] indicates that the activated polymer has more ordered structure than the reactants and the reactions are slower than normal. This is further supported by low Z value[25,26]. It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy [Ea] as decomposition mechanism is expected to be complicated. Positive values of activation energy under present investigation correspond to the energy of activation due oxidation – reduction process of terpolymer in the higher temperature range[27].

Fairly straight-line plots are obtained using the two methods. However, while using the Freeman- Carroll method some abnormal points were ignored to get a clear picture about most of the points. Similarly, in the Sharp- Wentworth method, some points at the beginning or at the end did not fall on straight line. This is expected, since, the decomposition of terpolymer is not obeying first order kinetics perfectly. These observations are in harmony with the findings of other earlier work[28].

Conclusion

The newly prepared terpolymeric ligand was found to be yellow coloured solid soluble in dimethylformamide and dimethylsulphonoxide having a melting point 578K. The thermogram exhibits single decomposition step (305-530°C). The decomposition temperature of MAF terpolymeric ligand is 390°C.Thermal activation energy (E_a) calculated by Sharp-Wentworth (21.10 KJ/mole) has been found to be in agreement with that calculated by Freeman-Carroll (21.46 KJ/mole) method.

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Table-6
Kinetic parameter of $[MAF]_n$ terpolymeric ligand

Terpolymeric Ligand	Entropy Change ΔS (J)	Free energy change ΔF (kJ)	Frequency factor Z (s^{-1})	Apparent entropy change S* (J)	Order of reaction (n)
$[MAF]_n$	-154.54	110.79	334.78	-203.26	0.83

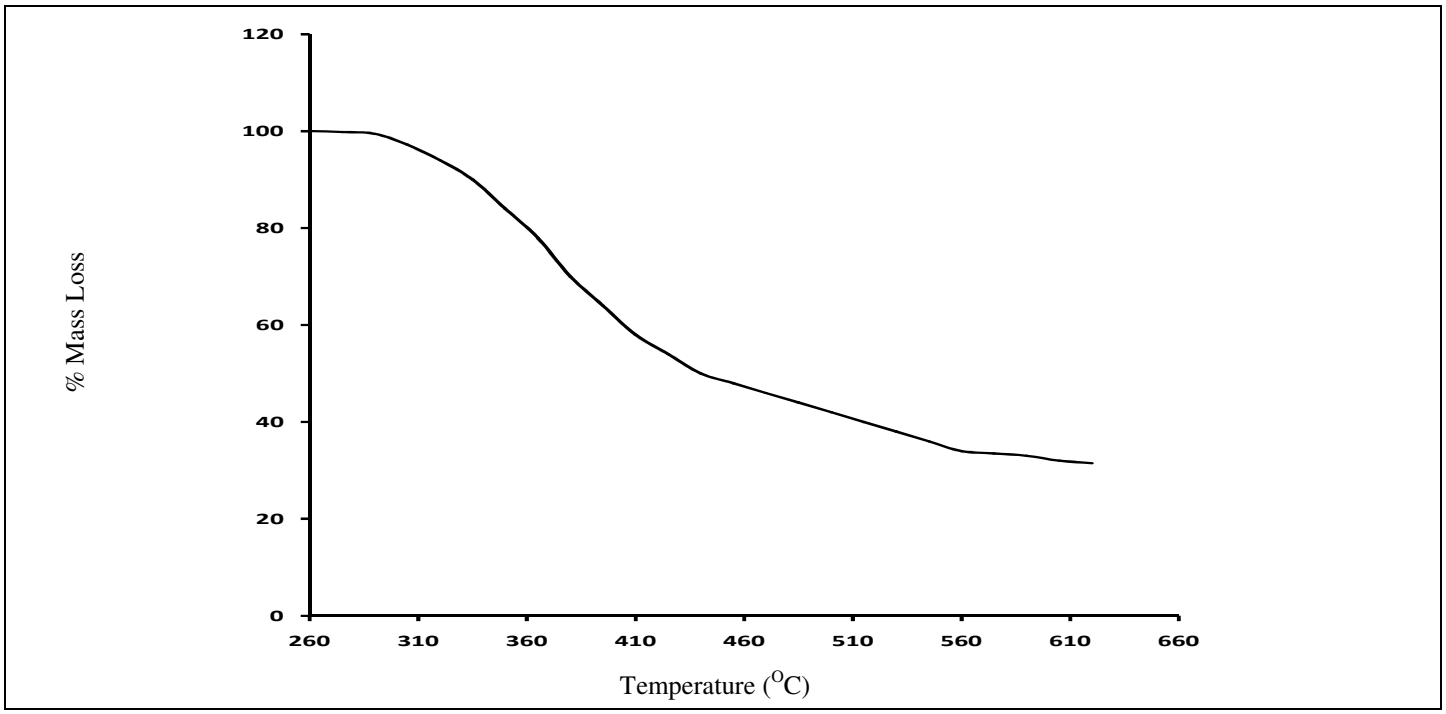

Figure-1
Thermogram of $[MAF]_n$

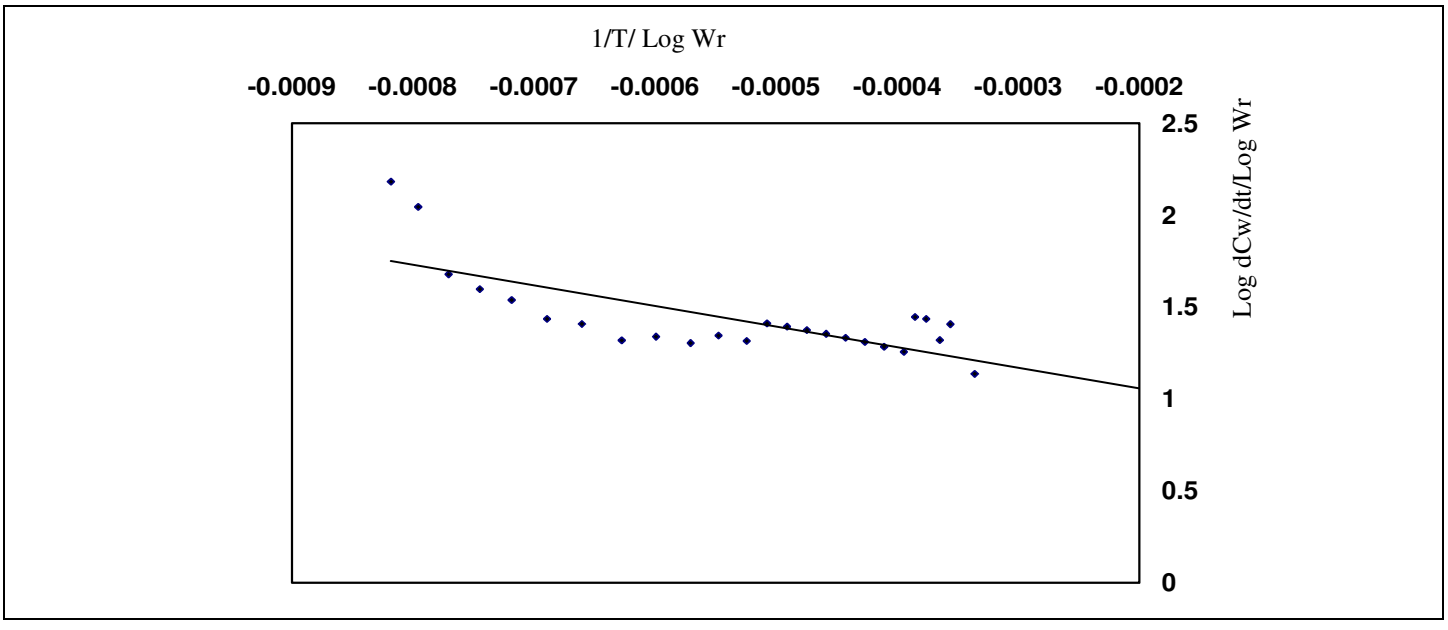

Figure-2
Freeman - Carroll plot for $[MAF]_n$ terpolymeric ligand

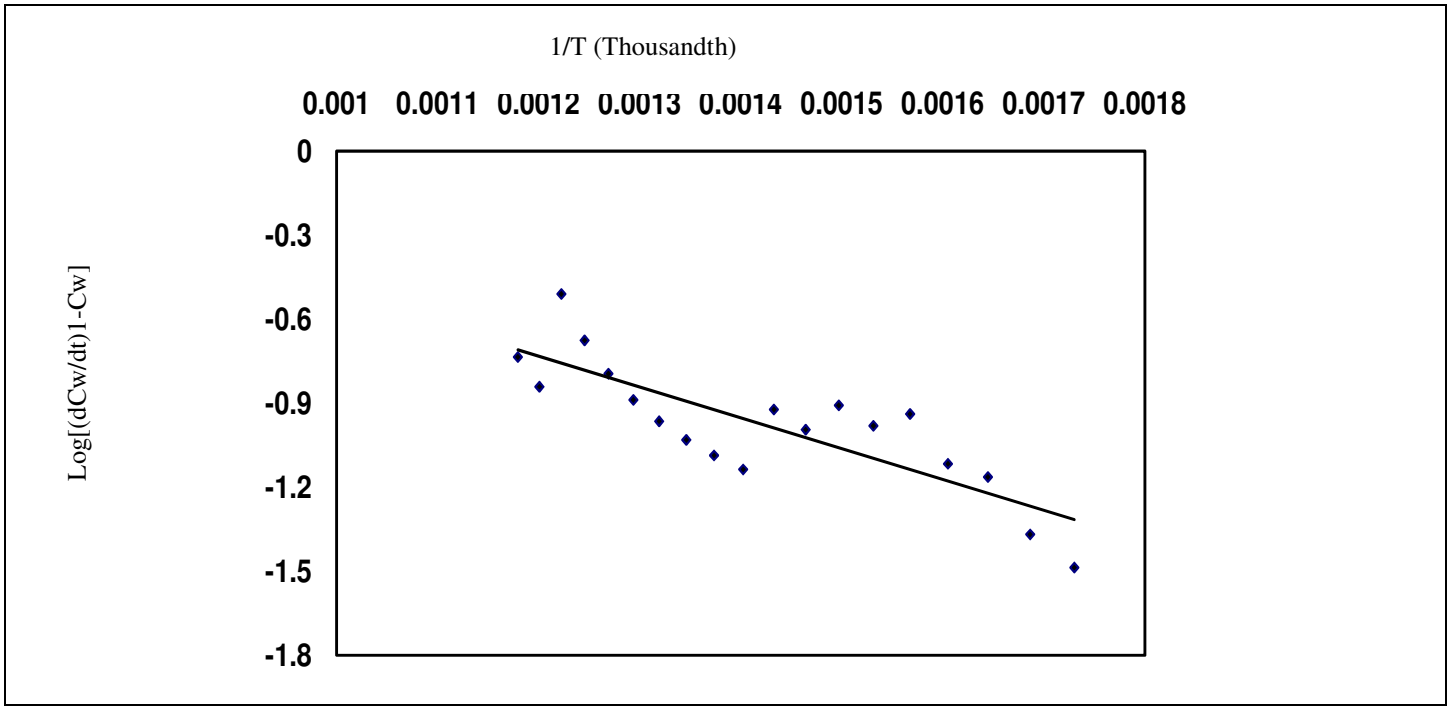

Figure-3
Sharp - Wentworth plot for $[MAF]_n$ terpolymeric ligand

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