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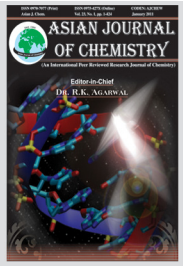

Synthesis, Characterization and Thermal Decomposition of *p*-Hydroxyacetophenone-aniline-formaldehyde terpolymeric Ligand

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Terpolymeric ligand, *p*-hydroxyacetophenone-aniline-formaldehyde (PAF) has been synthesized by the condensation of *p*-hydroxy acetophenone and aniline with formaldehyde 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}H NMR. Thermal decomposition curve shows single decomposition step (270-495 ºC). The Sharp-Wentworth and Freeman-Carroll methods have been used to calculate thermal activation energy and thermal stability. Thermal activation energy (E_a) calculated by Sharp-Wentworth (20.89 KJ/mol) method and Freeman-Carroll (21.08 KJ/mol) method are in good agreement. Thermal decomposition of the terpolymeric ligand has been carried out to determine their mode of decomposition, the activation energy (E_a), order of reaction (n), frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S*) on basis of Freeman-Carroll method.

Key Words: Decomposition, Sharp-Wentworth method, Freeman-Carroll method, Order of reaction, Entropy change, Apparent energy change.

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[1,2]. 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[3]. Various researchers have studied the applications of terpolymeric ligand of substituted phenols and formaldehyde[4,5]. Gurnule and coworkers have synthesizied and characterized terpolymers prepared from 8-hydroxyquinoline, biuret and formaldehyde[6] and from 4-hydroxyacetophenone-oxamide-formaldehyde[7].

Extensive work on the thermal degradation of terpolymers has been reported[8,9]. Thermogravimetric study of 8-hydroxy-quinoline-melamine-formaldehyde resin has also been carried out[10]. Terpolymer resins based on substituted *p*-cresol and melamine with formaldehyde have been synthesized and studied for its thermal properties by Singru *et.al.*[11].

The present communication deals with synthetic and thermal degradation properties of a newly synthesized terpolymeric ligand derived from *p*-hydroxyacetophenone and aniline with formaldehyde. The Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters[12-14]. Methods for the estimation of kinetic parameters from thermogravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible.

EXPERIMENTAL

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

Synthesis of polymeric ligand: For synthesis of terpolymeric ligand[15,16], a mixture of *p*-hydroxyacetophenone (0.05 mol), aniline (0.1 mol), formaldehyde (0.2 mol) in 200 mL HCl (2M) was refluxed on oil bath for 5-6 h 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 *p*-hydroxyacetophenone-aniline-formaldehyde was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel[17]. The sample and amount of reactant of *p*-hydroxyacetophenone-aniline-formaldehyde is given in Table-1.

TABLE-1
SAMPLE AND AMOUNT OF REACTANTS OF [*p*-HYDROXYACETOPHENONE-ANILINE-FORMALDEHYDE]$_n$ TERPOLYMERIC LIGAND

Reactants (mol)			Catalyst 2M HCl (aq.) (mL)	Reflux temp. ± 2 ºC	Molar ratio of reactant	Yield (%)	m.p. (K)
p-Hydroxy acetophenone	Aniline	Formaldehyde					
0.05	0.1	0.2	200	105	1:2:4	66	543

TABLE-2
ANALYTICAL DATA OF [*p*-HYDROXYACETOPHENONE-ANILINE-FORMALDEHYDE]$_n$ TERPOLYMERIC LIGAND

Terpolymeric ligand	Empirical formula	Elemental analysis (%): Found (calcd.)		
		C	H	N
[*p*-Hydroxyacetophenone-aniline-formaldehyde]$_n$	$C_{24}H_{24}N_2O_2$	77.21 (77.42)	6.43 (6.45)	7.51 (7.53)

The estimation of carbon, hydrogen and nitrogen was done by the elemental analyzers Elementar Vario EL III Carlo Erba 1108 from CDRI, 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 1 h using Bruker Avance II 400 NMR spectrometer at SAIF, Chandigarh (India). The spectra were recorded in (DMSO-d_6) solvent.

Thermogravimetric analysis (TGA) of polymer sample was carried out by using Perkin-Elmer diamond thermal analyzer at heating rate of 10 ºC/min and in air atmosphere up to 1000 ºC. The thermograms were recorded at Visvesvaraya National Institute of Technology, 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[18,19]. 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 expression (eqn. 1) is used to evaluate various kinetic parameters[20,21] like activation energy (E_a), entropy change (ΔS), free energy change (ΔF), frequency factor (Z), apparent entropy change (S*) and the order of reaction (n) of present compound.

$$\frac{\log \frac{dC_w}{dt}}{\log W_r} = \frac{-Ea}{2.303R} \cdot \frac{\frac{1}{T}}{\log W_r} + n \qquad (1)$$

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, dC_w/dt is the rate of change of weight with time and in expression $W_r = (W_c - W)$, W_c 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.

$$\log \frac{dC_w / dt}{1C_w} = \log(A/\beta) - \left[\frac{Ea}{2.303R}\right] \cdot \frac{1}{T} \qquad (2)$$

where, dC_w/dt is the rate of change of mass with time t, T is the temperature and $\beta = dT/dt$.

RESULTS AND DISCUSSION

The newly prepared terpolymeric ligand was found to be yellow coloured solid soluble in DMF and DMSO. The composition of terpolymeric ligand obtained on basis of elemental analysis data (Table-2) was found to be in good correlation to that of calculated values.

Key IR bands are given in Table-3. A broad band appearing in the region 3365 cm^{-1} is due to the stretching vibration of phenolic -OH group[22-26]. Presence of >NH has been indicated by the medium band at 2950 cm^{-1} which is merged with broad intense peak due to hydroxyl group[27,28]. The sharp band displayed at 1680 cm^{-1} may be on account of the stretching vibrations of carbonyl group(>C=O) of *p*-hydroxyacetophenone[29]. The inflections around 1450, 1285 and 780 cm^{-1} suggest the presence of bending, wagging, rocking vibrations of methylene (-CH_2-) bridges in polymeric chains[22,24,26]. The sharp peak at 1602 cm^{-1} may be due to aromatic skeletal ring. The band presence at 834 cm^{-1} may be due to tetra substituted benzene ring[22]. The bands at 1480 cm^{-1}, 758 cm^{-1} suggest the presence of -NH- bending, wagging in terpolymeric ligand respectively[26,28].

TABLE-3
IR SPECTRAL DATA OF [*p*-HYDROXYACETOPHENONE-ANILINE-FORMALDEHYDE]$_n$ TERPOLYMERIC LIGAND

Assignments	Observed band Frequency (cm^{-1})	Expected band Frequency (cm^{-1})
Phenolic -OH	3365	3500-3000
>NH stretch	2950	3500-2800
>C=O stretching	1680.9	1690-1630
Phenolic C-O	1376.6	1410-1310
Methylene bridge (-CH_2-) mode	1285.5 (w)	1300-1200
	1450.5 (b)	1460
	780.7 (r)	775
Tetra substitution benzene ring	834.8	~830
N-H wagging	758.8	650-800
N-H bending	1480.8	1490-1570

The NMR spectrum of the *p*-hydroxyacetophenone-aniline-formaldehyde terpolymeric ligand exhibited signal in the region of 6.34-7.36 δ (ppm), which may be due to the proton of the aromatic rings (Ar-H) and the signal in the region 8.85 δ (ppm) can be assigned to the phenolic-OH proton in hydrogen bonding[26,29,30]. The presence of a signal around 2.48 δ (ppm) may be due to the methyl proton[31] of Ar-CO-CH_3. The presence of a broad signal around 6.89 δ (ppm) is attributed to the presence of -NH bridges[26,30]. A methylene proton Ar-CH_2-Ar appearance of a weak singlet signal at 3.55 δ (ppm)[32,33]. The spectral data is as tabulated in Table-4.

TABLE-4
^{1}H NMR SPECTRAL DATA OF [*p*-HYDROXYACETOPHENONE-ANILINE-FORMALDEHYDE]$_n$ 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
Phenolic (Ar-OH)	8.85	7.5-12
Ar-CO-CH_3	2.48	2.38-2.55
-NH bridging	6.89	5.4-8.5
Ar-CH_2-Ar	3.55	2.7-4.3

Thermogravimetric studies of *p*-hydroxyacetophenone -aniline-formaldehyde: Thermogravimetric analysis of *p*-hydroxyacetophenone-aniline-formaldehyde has been carried out and thermogram and kinetic plots for *p*-hydroxyacetophenone-aniline-formaldehyde are given in Figs. 1-3. The thermogram exhibits single decomposition step (270-495 ºC).

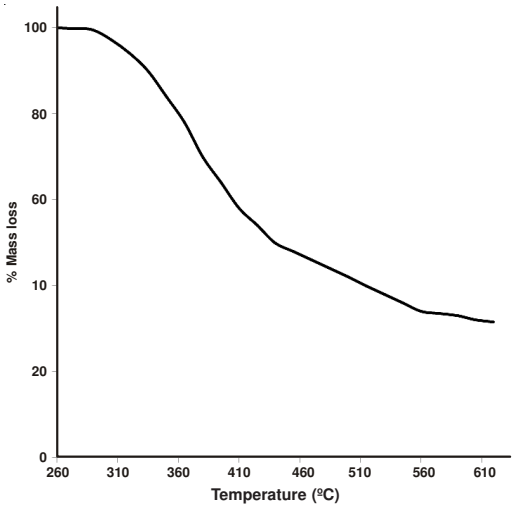

Fig. 1. Thermogram of [*p*-hydroxyacetophenone-aniline-formaldehyde]$_n$

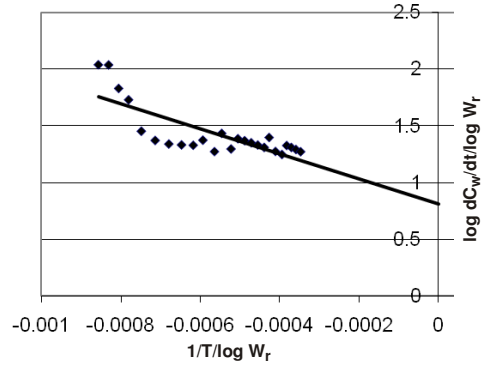

Fig. 2. Freeman-Carroll plot for [*p*-hydroxyacetophenone-aniline-formaldehyde]$_n$ terpolymeric ligand

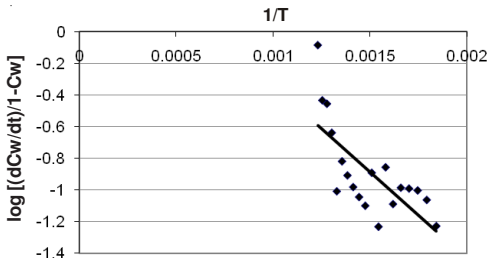

Fig. 3. Sharp-Wentworth plot for [*p*-hydroxyacetophenone-aniline-formaldehyde]$_n$ terpolymeric ligand

The thermal degradation curve of *p*-hydroxyacetophenone-aniline-formaldehyde shows that there is no mass loss up to 270 ºC due to absence of water of hydration and water of coordination. From 270 to 495 ºC gradual mass loss is observed may be due to degradation of polymer. After 495 ºC no mass loss is observed indicates stable species formation. The decomposition temperature of *p*-hydroxyacetophenone-aniline-formaldehyde is 330 ºC. (Total mass loss (%): calcd. 82.19, obs. 81.00).

Thermogram of *p*-hydroxyacetophenone-aniline-formaldehyde terpolymeric ligand shows activation energy calculated (Table-5) by the Freeman-Carroll and Sharp-Wentworth methods are in good agreement with each other.

TABLE-5
ACTIVATION ENERGY AND DECOMPOSITION TEMPERATURE OF [*p*-HYDROXYACETOPHENONE-ANILINE-FORMALDEHYDE]$_n$ TERPOLYMERIC LIGAND

Terpolymeric ligand	Decomposition temperature (ºC)	Activation energy (kJ/mol)	
		Freeman-Carroll	Sharp-Wentworth
[*p*-Hydroxyacetophenone-aniline-formaldehyde]$_n$	330	21.08	20.89

Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table-6. Due to 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[34,35]. It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy [E_a] 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[32].

TABLE-6
KINETIC PARAMETER OF [*p*-HYDROXYACETOPHENONE-ANILINE-FORMALDEHYDE]$_n$ TERPOLYMERIC LIGAND

Entropy change ΔS (J)	-154.10
Free energy change ΔF (kJ)	104.76
Frequency factor Z (s^{-1})	337.12
Apparent entropy change S* (J)	-202.41
Order of reaction (n)	0.81

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 Jacobs and Tompkin and other earlier workers[36].

Conclusion

The newly prepared terpolymeric ligand was found to be yellow coloured solid soluble in DMF and DMSO having a

melting point 543 K. The thermogram exhibits single decomposition step (270-495 ºC). The decomposition temperature of *p*-hydroxyacetophenone-aniline-formaldehyde terpolymeric ligand is 330 °C. Thermal activation energy (E_a) calculated by Sharp-Wentworth (20.89 KJ/mol) has been found to be in agreement with that calculated by Freeman-Carroll (21.08 KJ/mol) method.

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REFERENCES

1. T.M. Machrnudov, S. Abudullaev and K.S. Adhmedov, *Doki. Nauk. USSR*, **27**, 34 (1970).
2. J.S. Parmar, M.M. Patel and M.R. Patel, *Angew. Makromol. Chem.*, **93**, 11 (1985).
3. M. Jadhao, L.J. Paliwal and N.S. Bhave, In Thermans XIV National Symposium & Workshop Vadodara, India, p. 250 (2004).
4. A.P. Das, S. Lenka and P.L. Nayak, *J. Appl. Polym. Sci.*, **30**, 4619 (1985).
5. R.K. Samal and B.K. Senapati, *J. Appl. Polym. Sci.*, **62**, 655 (1996).
6. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal and R.B. Kharat, *React. Funct. Polym.*, **55**, 255 (2003).
7. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal and R.B. Kharat, *Prog. Cryst. Growth Charac. Mater.*, **45**, 127 (2002).
8. S.S. Rahangdale, A.B. Zade and W.B. Gurnule, *J. Ultra. Sci.*, **19**, 213 (2007).
9. M.V. Tarase, A.B. Zade and W.B. Gurnule, *E.-J. Chem.*, **6**, 639 (2007).
10. W.B. Gurnule, H.D. Juneja and L.J. Paliwal, *Orient. J. Chem.*, **15**, 283 (1999).
11. R.N. Singru, A.B. Zade and W.B. Gurnule, *J. Appl. Polym. Sci.*, **109**, 859 (2008).
12. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
13. E.S. Freeman and D.A. Anderson, *J. Polym. Sci.*, **54**, 253 (1961).
14. J.B. Sharp and S.A. Wentworth, *J. Anal. Chem.*, **41**, 2060 (1969).
15. V.V. Hiwase, A.B. Kalambe, K.M. Khedkar and S.D. Deosarkar, *E-J. Chem.*, **7**, 287 (2010).
16. W.B. Gurnule, H.D. Juneja, L.J. Paliwal, *Prog. Cryst. Growth Charact. Mater.*, **45**, 155 (2002).
17. M.M. Patel and R.J. Manavaian, *Indian Chem. Soc.*, **61**, 490 (1984).
18. D.T. Masram, K.P. Kariya and N.S. Bhave, *e-Polymers*, 75 (2007).
19. M. Jadhao, L.J. Paliwal and N.S. Bhave, *J. Appl. Polym. Sci.*, **96**, 1605 (2005).
20. V.V. Ukey, H.D. Juneja, S.D. Borkar, R.S. Gubde and S. Naz, *J. Mater. Sci. Eng. B*, **132**, 34 (2006).
21. P.E.P. Michael, J.M. Barbe, H.D. Juneja and L.J. Paliwal, *Eur. Polym. J.*, **43**, 4995 (2007).
22. Organic Spectroscopy, W. Kemp, The MacMillan Press, Hong Kong Press (1975).
23. S. Meenakshi and N. Vishwnathan, *J. Colloid. Interface Sci.*, **308**, 438 (2007).
24. B. Singh and N. Sharma, *J. Polym. Degrad. Stab.*, **1**, 19 (2007).
25. G.E. Dunn and R.C. McDonald, *Can. J. Chem.*, **47**, 4577 (1969).
26. K. Nakanishi, Infrared Absorption Spectroscopy Practical, Nolden Day and Nankod, Tokyo (1967).
27. H.H. Willard, L.I. Merrit, J.A. Dean and F.A. Seattle, Instrumental Methods of Analysis, CBS: New Delhi (1986).
28. P.S. Kalsi, Spectroscopy of Organic Compounds, New Age International, New Delhi, edn. 2 (1995).
29. J.R. Dyer, Application of Absorption Spectroscopy of Organic and Biological Chemistry, MIR: Moscow (1975).
30. A.I. Vogel, Textbook of Practical Organic Chemistry, Longman Scientific and Technical, UK (1989).
31. H.-Y. Ma, Y. Sun, Y.-Z. Zhou, M. Hong and Y.-H. Pei, *Molecules*, **13**, 267 (2008).
32. T.K. Pal and R.B. Kharat, *Indian J. Chem.*, **22A**, 55 (1989).
33. R.M. Silverstein and G.C. Bassler, Spectrometric Identification of Organic Compounds, John Wiley, New York, edn. 2 (1967).
34. A.W. Coats and J.P. Redfen, *Nature*, **201**, 68 (1964).
35. T. Ozawa, *J. Thermal Anal.*, **7**, 601 (1985).
36. P.W.M. Jacobs and F.C.Tompkins, Chemistry of Solids State, E.G Garner Publication, London, p. 188 (1955).