Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2011, 3 (5): 128-134
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Thermal Study of the newly synthesized organic polymer 8-HQ5-SAOF-II

R. N. Singru

Department of Chemistry, R.D College of Science, Aheri, Gadchiroli, Maharashtra, India

---

ABSTRACT

The title terpolymer (8-HQ5-SAOF-II) synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid (8-HQ5-SA) and oxamide (O) with formaldehyde (F) in the presence of acid catalyst and using 2:1:3 molar proportion of the reacting monomers. The morphology of synthesized terpolymer was studied by scanning electron microscopy (SEM). The thermogravimety of the terpolymer resin prepared in present study has been carried out by non-isothermal thermogravimety technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resin was carried out to determine the mode of decomposition and relative thermal stability. Thermal decomposition curve was studied carefully with minute details. The Freeman-Carroll and Sharp-Wentworth methods have been used in the present investigation to calculate thermal activation energy and different kinetic parameter of the terpolymer resin. The advantage of Freeman-Carroll method is to calculate both the order of reaction/ n and energy of activation in one single stage by keeping heating rate constant. By using data of thermogravimety, various thermodynamic parameters like frequency factor/ Z, entropy change/ ΔS, free energy change/ΔF and apparent entropy/ S have been determined using Freeman-Carroll method.*

Keywords: Decomposition, polycondensation, resins, Synthesis, thermogravimetric analysis.

INTRODUCTION

Terpolymers are useful materials in fabrication, flexibility, chemical inertness as well as being light in weights. Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are investigated as the materials of electronics [1, 2], opto-electronics [3, 4] and photonics [5]. In addition, electrically conducting polymers have a wide variety of applications ranging from electrode materials [6], microelectronic devices [7], catalysts for photo-electrochemical processes [8], organic batteries [9] to electrochemical display devices [10]. The oxidative polycondensation method is simply the reaction of compounds including –OH groups and active functional groups (–NH2, –CHO, –COOH) in their structure with the oxidants as NaOCl, H_2O_2, and air in the aqueous alkaline and acidic medium [11]. Another class of this family is that of polyamines (PIs), which are also known as polymeric Schiff bases, polymers that are synthesized by a polycondensation reaction

between an amine and hydrazine with an aldehyde or diketone [12]. Because of the properties based on their electronic structure, oligophenols, they have paramagnetism, semi-conductivity, electrochemical cell and resistance to high energy. Therefore, they have been used to prepare composites with resistance to high temperature and graphite materials, epoxy oligomer and block copolymers, adhesives, photoresists and antistatic materials [13-14]. Schiff based derivatives of oligophenols have and electrochemical properties of some poly (Schiff) bases and their metal complexes have been studied by Kaya et al. [15, 16]. Poly (*p*-phenylene-2, 6-benzoxazole) (PBO) fiber, which is a new kind of high performance rigid-rod isotropic crystal polymers, has excellent thermal stability, solvent resistance, remarkable tensile strength and modulus [17, 18].

The present paper describes thermal analysis of the newly synthesized resin of 8-hydroxyquinoline 5-sulphonic acid (8-HQ5-SA) and oxamide (O) with formaldehyde (F),by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation/*Ea*, thermodynamic parameters viz. *Z*, *ΔS*, *ΔF*, *S**, and order of reaction/ *n* were determined by applying Freeman-Carroll Method.

MATERIALS AND METHODS

Materials

The entire chemical used in the synthesis of various new terpolymer resins were procured from the market and were analar or Fluka or chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, reprecipitation and crystallization which are generally used for the analytical purification purpose.

Synthesis of 8-HQ5-SAOF-II terpolymer resins

The new terpolymer resin 8-HQ5-SAMF-II was synthesized by condensing 8-hydroxyquinoline 5-sulphonic acid (0.2 mol) and oxamide (0.1 mol) with 37% formaldehyde (0.3 mol) in a mol ratio of 2:1:3 in the presence of 2 M 200 ml HCl as a catalyst at 130 ^{0} C ± 2 ^{0} C for 6h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated terpolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 8-hydroxyquinoline 5-sulphonic acid formaldehyde copolymer which might be present along with 8-HQ5-SAOF-II terpolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 8-HQ5-SAOF-II in shown in Fig. 1.

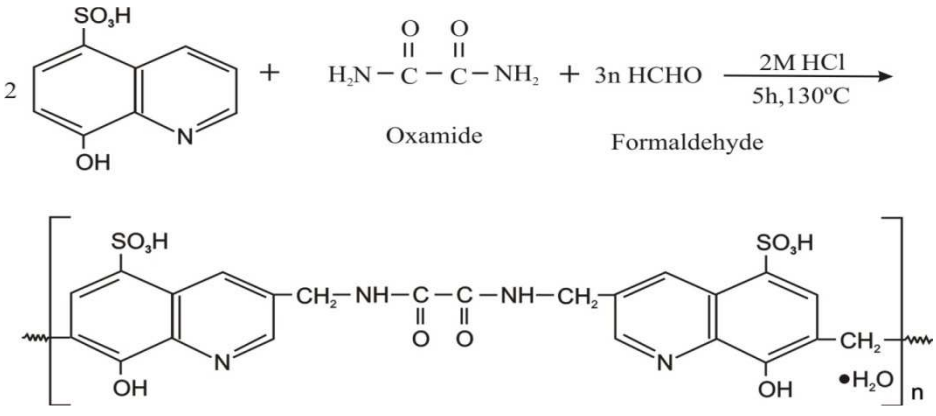


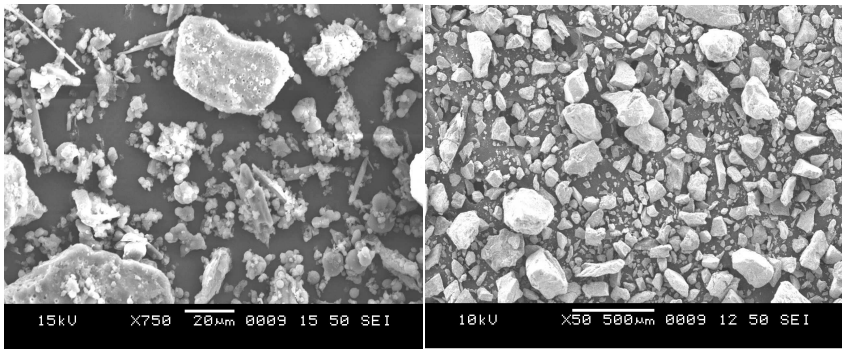
Fig. 1: Synthesis and structure of 8-HQ5-SAOF-II terpolymer resin

The terpolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The terpolymer sample 8-HQ5-SAOF-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the terpolymer resin was found to be 75%.

RESULTS AND DISCUSSION

The newly synthesized purified 8-HQ5-SAOF-II terpolymer resin was found to be yellow in color. The terpolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents.

SEM micrographs of 8-HQ5-SAOF-II terpolymer are shown in Fig.2.The morphology of pure sample shows spherulites with deep pits. This is the transition of crystalline and amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structures at the beginning of the reaction but during course of condensation polymerization the crystalline structures of monomers lost into amorphous nature in terpolymer resin [19].



(A) **(B)**

Fig.2: SEM micrographs of 8-HQ5-SAOF-II terpolymer resin

Thermogravimetry:

A brief account of thermal behavior of 8-HQ5-SAOF terpolymer has been given in Fig. 3-5.

TG of 8-HQ5-SAOF-II terpolymer:

Decomposition curve of this terpolymer has shown in Fig. 3 in the temperature range of 40ºC to 800ºC, showing three stage decomposition pattern with initial weight loss of one water molecule (3.00% found and 3.04% calculated) in the temperature range of 40ºC to 140ºC. In the first stage of decomposition there is gradual mass loss from temperature range of 140ºC to 300ºC corresponding to mass loss of 36.11% found against 36.14% calculated. The degradation may be due to two hydroxyl groups and two sulphonic groups attached to aromatic quinoline ring, due to increasing strained and unstability in the molecule by increasing thermal vibrations due to increasing temperature. In the second stage, the cross linking sits develop a more strain in the macromolecule with result a rapid mass loss from temperature range of 300ºC to 510ºC, corresponding mass loss of 81.21% found and 81.75% calculated. The degradation may be due to two aromatic quinoline rings. In the third stage of decomposition, the strained molecule suffer high cross linking, occurs depolymerization, leads to gradual mass loss from temperature range of 510ºC to 800ºC, corresponding the mass loss 99.56% found and 100.00% calculated, up to the end of decomposition reaction which may be due to loss of oxamide moiety and its side chain. The residue left over after complete degradation was found to be negligible.

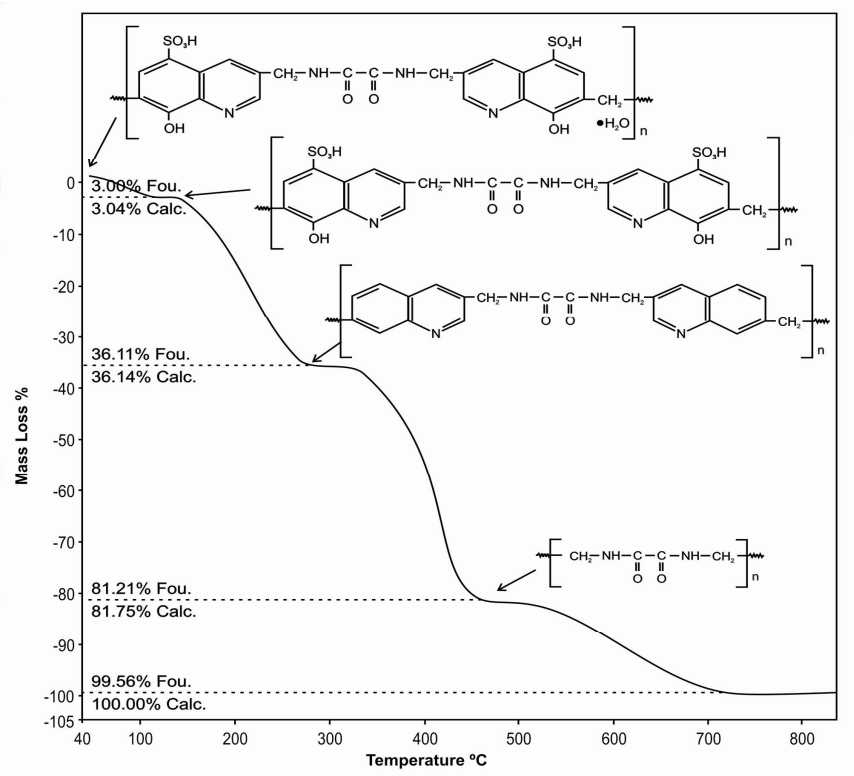


Fig. 3 Decomposition Pattern of 8-HQ5-SAOF-II Terpolymer Resin

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been used to determine the thermodynamic parameters of 8-HQ5-SAMF-II terpolymer sample.

Sharp-Wentworth method:
In this method following expression is used.

$$\log dc/dT/(1\text{-}C) = \log \acute{\alpha}/\beta = Ea/2.303RT$$

Where, β is the linear heating rate. The graph of log dc/dT/ (1-C) versus 1/T on 'X' axis has been plotted. The graph is a straight line with Ea as slope and A as intercept on 'Y' axis. The linear relationship confirms that the assumed order/n = 1 is correct.

Freeman-Carroll method: In this method following expression is used.

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

Where, dw/dt = rate of change of mass of terpolymer sample with respect to time $Wr = Wc\text{-}W$, where Wc is the mass loss at the completion of the terpolymer reaction or at definite time and W is the total mass loss up to time t. T is the temperature, R is the gas constant and n is the order of reaction. Hence the graph of,

$\Delta \log (dw/dt) / \Delta \log Wr$ versus $\Delta (1/T) / \Delta \log Wr$

Should give the value of the order of reaction n on 'Y' axis and the slope $m = -Ea/2.303R$. The detailed procedure is clearly laid out for one representative sample as an illustration.

A plot of percentage mass loss versus temperature (thermogram) is shown in Fig. 3 for 8-HQ5-SAOF-II terpolymer. From the TG curves, the thermo analytical data and the decomposition temperature was determined to obtain the relative thermal stability of the terpolymer. The methods described by Sharp –Wentworth and Freeman-Carroll ware adopted.

Using thermal decomposition data and applying the Sharp-Wentworth method, activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method [20].The activation energy/ *Ea* can be calculated by using equation Slop = - *Ea/2.303R* Where, *R* is the gas constant and slop can be calculated from the corresponding plots of Sharp-Wentworth method and Freeman-Carroll method.

A representative thermal activation energy plot of Sharp-Wentworth method (Fig.4) and Freeman-Carroll method (Fig.5) for the polymer have been shown. Thermodynamic parameters such as entropy change/*ΔS*, free energy change/*ΔF*, frequency factor/*Z* and Apparent entropy/ *S** calculated on the basis of thermal activation energy are given in Table 1, using equations are given below.

(i) Entropy change

Intercept = log $KR/ H \Phi E+ \Delta S/2.303R$

Where,
$K = 1.3806 \times 10^{-16}$ */J deg-1 mole-1*
R = 8.314 /J deg-1 mole-1
$h = 6.625 \times 10^{-27}$ */J sec*
Φ = 0.166
ΔS= change in entropy
E = activation energy from graph

(ii) Frequency factor

$B_{2/3}$ = log $Z Ea / R \Phi$----------[1]
$B_{2/3}$ = log 3 + log [1-3] √ (1- ά) – log P(x)—[2]

Where,
Z = Frequency factor
B = Calculated from equation[2]
Log p(x) = Calculated from Doyle table corresponding to activation energy

(iii) Free energy change

$\Delta F = \Delta H - T\Delta S$

Where,
ΔH = Enthalpy change = Activation energy
T = Temperature / K
ΔS = Entropy change {from (i) used}

(iv) Apparent entropy change

$S^* = 2.303 \log Zh / RT^*$----------[3]

Where,
Z = from relation [1]
*T** = Temperature at which half of the compound is decomposed from it total loss**.**

The 8-HQ5-SAOF-II terpolymer prepared from higher molar ratio of 8-hydroxyquinoline 5-sulphonic acid exhibited a lower rate of decomposition. This order of stability may be due to the possibility of an almost linear structure of the terpolymer having higher molar ratio of 8-hydroxyquinoline 5-sulphonic acid which may give rise to a stable structure to the terpolymer chain [20, 21]. In the present study, in case of 8-HQ5-SOMF-II terpolymer the removal of water from the polymer is completed around 140 ^{0} C, which may be due to solvent or moisture probably crystal water entrapped in the terpolymer samples [22, 23].

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 1). From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 8-HQ5-SAMF-II terpolymer can be classed as a 'slow' reaction which can also be supported by negative value of entropy change. There is no other obvious reason [24, 25,26].

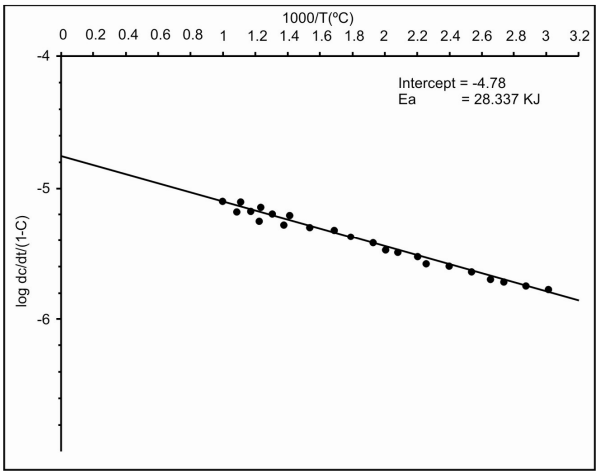


Fig. 3 Sharp-Wentworth plot of 8-HQ5-SAOF-II Terpolymer Resin

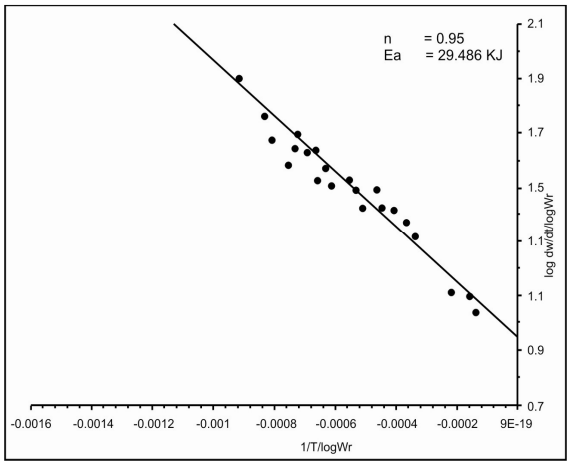


Fig. 3 Freeman-Carroll plot of 8-HQ5-SAOF-II Terpolymer Resin

Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is not to obey first order kinetics perfectly.

Table 1 Result of Thermogravimetric Analysis of 8-HQ5-SAOF terpolymer resin

Terpolymer Resins	Half decomposition temp, T_h/ K	Activation energy/ KJmol^{-1}		Entropy change $-\Delta S$ (J)	Free energy change ΔF/KJ	Frequency factor Z/ sec^{-1}	Apparent entropy S*/ J	Order of reaction found/n
		FC*	SW*					
8-HQ5-SAOF-II	613	24.508	23.167	-160.698	97.304	746	-19.032	0.95

**FC = Freeman-Carroll, *SW = Sharp-Wentworth*

CONCLUSION

1) A terpolymer, 8-HQ5-SAMF-II, based on the condensation reaction of 8-hydroxyquinoline 5-Sulphonic acid-Melamine-formaldehyde in the presence of acid catalyst, was prepared.
2) Low values of collision frequency factor (Z) may be concluded that the decomposition reaction of 8-hydroxyquinoline 5-sulphonic acid-melamine-formaldehyde terpolymer can be classified as 'slow reaction'.
3) The decomposition reaction was started at higher temperature, indicating a terpolymer 8-HQ5-SAMF-II is thermally stable at higher temperature.

Acknowledgement
The authors are grateful to Director and Head, Department of Chemistry, L.I.T., R.T.M. Nagpur University, Nagpur, for providing laboratory facility. We are also thankful to the Director, SAIF, Punjab University; Chandigarh.

REFERENCES

[1] F.R. Diaz, J. Moreno, L.H. Tagle, G.A. East, D. Radi, *Synth Met*,100(**1999**)187-93.
[2] S.C. Suh, S.C. Shim, *Synth Met*, 114(**2000**)91-5.
[3] J.L. Bredas, R.R. Chance, Kluwer Academic, Dordrecht; the Netherlands: **1990**.
[4] S.R. Marder, J.R.Sohn, G.D. Stucky, Materials for Non-linear Optics: Chemical Perspectives. ACS. Washington; DC: **1991**.
[5] I. Ledoux-Rak, A. Dodabalapur, P. Blom,*Synth Met* , 127(**2002**)1-2.
[6] A.l. Shawabkeh, H.A. Wahab, Y.A. Shahab, *J Optoelectron Adv Mater* 9(**2007**)2075-77.
[7] H. Nishide, N. Yoshioka, E. Tsuchida, H.Inoue, *J Polym Sci Part A: Polym Chem* 27(**1989**)497-505.
[8] M. Mazur, A.M. Kaminska, J Bukowska, *Electrochimica Acta, 52(* **2007**)5669-76.
[9] R.K. Gupta, R.A. Singh, *J Polym Res,* 12(**2005**)189-95.
[10] E.P. Koval'chuk, N.V. Stratan, O.V. Reshetnyak, J. Blazejowski, M.S. Wittingham, *Solid State Ionics,* 141(**2001**)217-24.
[11] M.Y. Khuhawar, A. Shah, M.A. Mughal, *J Polym Sci* , 25(**2007**)399-407.
[12] I.Cianga, M.Ivanoiu, *Eur Polym J,* 42(**2006**)1922-33.
[13] C. Racles, V. Cozen, I. Sajo, *High Perform Polym, 19(* **2007**)541-52.
[14] G. Bereket, E. Hur, Y.Sahin, *Prog Org Coat*, 54(**2005**)63-72.
[15] I. Kaya, H.O. Demir, A.R. Vilayetoglu. *Synth Met* , 126(**2002**)183- 191.
[16] I. Kaya, S.Koyuncu, *Polymer, 44(* **2003**)7299-309.
[17] L.. Guan, C.X.Zhang, *Polym Degrade Stab* , 84(**2004**)369-73.
[18] Y. Imai, K. Itoya, M. Kakimoto, *Macromol Chem Phys* , 201(**2000**)2251-56.
[19] P.K. Rahangdale, W.B.Gurnule, L.J. Paliwal, R.B. Kharat, *Proceeding of National Conference on Recent Trends in Nanoscience.* **2006**; 222.
[20] W.B. Gurnule, H.D. Juneja, L.J. Paliwal. *Asian J Chem*, 11(**1999**)767-73.
[21] W.B. Gurnule, H.D. Juneja, LJ. Paliwal. *Proceeding of International Congress of Chemistry and Environment, Indore.* **2001**; 98-101.
[22] S.S. Katkamwar, A.B. Zade, W.B. Gurnule. *J Ultra Scientist of Physical Sciences,* 73(2) (**2008**)103-108.
[23] M.V. Tarase, A.B. Zade, W.B. Gurnule. *J Ultra Chemistry*, 23(1)(**2007**)41-48.
[24] M.K. Tamargo, R.S. Villar, J.I. Paredes, *Chem Mater, 15 (***2003**)4052-59.
[25] C.A. Nielsen, P. Pierini, S. Fuh, *J Fire Sci,* 11(**1993**)56-71.B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A. R. Tatchell. Vogel's Text Book of Practical Organic Chemistry. Addison Wesley Longman Ltd: England; **1998**.