SYNTHESIS AND THERMAL STUDIES OF MULTIFUNCTIONAL MATERIAL DERIVED FROM 2, 6- DIHYDROXY ACETOPHENONE, PARAPHENYLENEDIAMINE AND FORMALDEHYDE

S. N. Niley[1], K. P. Kariya[2] and B. N. Berad[3]

[3]Department of Chemistry, Rastrasant Tukadoji Maharaj, Nagpur University, Nagpur-440033, India
[2]Department of Chemistry, VMV Com. JMT Arts & JJP Science College, Nagpur 440008, India
[1]Department of chemistry, Guru Nanak College, Ballarpur, India
sanjaynileyresearch@gmail.com

Abstract:
Terpolymeric material was synthesized by the condensation of 2,6-dihydroxy acetophenone, paraphenylenediamine, and formaldehyde in the presence of acid catalyst with 1:1:2 molar ratio of reacting monomers. The polymer has been characterized by UV–visible, IR and ^{1}H-NMR spectra. Thermal degradation curve has been discussed in order to determine its mode of decomposition, order of reaction, apparent activation energy, frequency factor and free energy change. Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters while the data from the Freeman-Carroll method have been used to determine various thermodynamic parameters. This polymer is also found to possess optimum antibacterial activities.
Keywords: : Synthesis, Characterization, Thermal Studies

Introduction

The use of terpolymers in all spheres of life has been abundantly increased in recent years because of novelty and versatility. They occupy the pivotal position in the field of polymer science. The progress in this field has been extremely rapid as they are generally useful in packaging, adhesives, coatings, in electrical sensors,ion-exchangers, organometallic semiconductors, activators, catalysts and thermally stable materials[1]. Due to global applications of polymeric materials, polymer science and technology have been developing rapidly and attracted much attention of polymer scientists. Polymers have been found to be very useful applications as adhesives, high temperature flame-resistant fibers, coating materials, semiconductors, catalysts, and ion exchange resins [2]. Varieties of researches regarding the thermal studies of polymers are emerging out to investigate their renewed applications for the betterment of mankind. Area of polymer reaction kinetics is enhanced by applying various model fitting kinetic equations in order to study its kinetic and thermodynamic aspects [3]. Much attention has been focused to synthesize the terpolymers by applying various synthetic techniques to examine its advanced applications. In the recent past, appreciable progress has been made in study of many ternary systems such as acrylonitrile-methylmethacrylate-methacrylic acid [4]. methylmethacrylate-styrene-butadiene [5] acrylonitrile-methyl acrylate-itaconic acid [6], styrene-acrylonitrile-methyl- acrylate [7]. Jadhav et.al studied synthesis, characterization, and thermal degradation kinetics of copolymers derived from 2,2'-dihydroxybiphenyl-formaldehyde [8]. kinetics of thermal degradation and estimation of lifetime for polypropylene particles and its effect on particle size, involving the use of single, and multiple heating rate techniques was studied by Paik et.al. [9].

Materials And Methods

All the chemicals used in the synthesis of new terpolymer resin were procured from the market and were of 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.

Preparation of Sample

A mixture of 2,6-dihydroxyacetophenone (0.1 mol), Paraphenylenediamine (0.1 mol) and formaldehyde (0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst has been prepared in round bottom flask. The resultant mixture was refluxed over an oil bath for heating at 120ºC ± 2ºC for 5 hrs with occasional shaking to ensure thorough mixing. The resinous yellowish solid mass was obtained.

Results And Discussion

Characterization of synthesized resin

The electronic spectrum of 2,6-DHAPDF-I is shown in (fig.2). The spectra depicted two characteristic bands. The band at 255nm indicates the presence of (>C=O) group containing C-O double bond in conjugation with an aromatic nucleus and can be accounted for π π* transition. The other less intense band at 355 nm may be due to n π* electronic transition [10]. The IR spectra was shown in (Fig.3). The assignment of Vibrational frequencies is based on

the data available in the literature. A broad band appeared at 3286.90 cm-1 might be due to the stretching vibrations of phenolic hydroxyl group exhibiting intermolecular hydrogen bonding which exist between OH grops of different polymer chain. The medium band at 3100 cm-1 is assigned to the –NH stretching vibration. The band obtained in the range of 1439.2, 1334.5 and 812.14 cm-1 is ascribed to bending , wagging and rocking vibrations of methylene (-CH2-) bridges. The band in the range of 1245 is due to (C-N) stretching. The medium broad band in the range of 694-892.18 is attributed to substituted benzene ring. The band at 1705 cm-1

may be due to the >C=O stretching. The band at 1370.30 cm-1 may be ascribed to phenolic C-O stretching. The NMR spectra of 2,6-DHAPDF-I terpolymer was shown in Fig.4 .The NMR spectrum of the 2,6-DHAPDF-I terpolymer exhibits signals in the region of 6.84 δ (ppm), which may be due to the proton of aromatic ring (Ar- H), and signals in the region 11.09 δ (ppm) may be attributed to phenolic hydroxyl proton , methylene proton Ar-CH2-N moiety was inferred by the appearance of a weak singlet signal at 3.58-3.63 δ (ppm). The presence of a signal around 6.31 δ (ppm) revels the presence of –NH bridges. Methyl proton of Ar-Co-CH3 moiety may be identified by the intense peak in the region of 2.51 δ (ppm).

The thermal degradation curve for the 2,6-DHAPDF-I terpolymer is shown in Fig. 5. Thermogram of 2,6-DHAPDF-I, depicted only one stage of decomposition without loss of water molecule. The first step of decomposition in the range of 200-600 0C was due to loss of side chain (-CH2-NH-Ar-NH-,COCH3,2OH,-CH2) and partial degradation of aromatic nucleus (Calc = 95.02 % and Found = 94.00 %) first stage of decomposition supported by exothermic peak in DTA [Fig.6]. Using half decomposition data and then applying the Sharp-Wentworth method[11], we obtained a Sharp-Wentworth plot for terpolymer as shown in Fig. 7. Ea calculated by this method was in agreement with the Ea calculated by Freeman-Carrol method [12], A thermal Ea plot and Freeman-Carrol plot for polymer is shown in Fig. 8 and 9 respectively. The thermodynamic parameters for the polymer were calculated on the basis of thermal Ea values, which are shown in Table-2.

From the data in Table-2. from the abnormally low values of the frequency factor we concluded that the decomposition of 2,6-DHAPDF-I polymer can be classified as a slow reaction for which there is no other obvious reason [13-16]. The negative value of [ΔS] indicate that the activated polymer has more ordered structure than the reactants and that the reaction are slower, than normal . The decomposition of terpolyerm is known to obey first-order kinetics but not perfectly, as by Shrivastava and Juneja .

Table-1-Thermal degradation data of 2,6-DHAPDF-I Terpolymer

Terpolymer	Temperature Range (0C)	Stage of Decomposition (DTA Peak)	Species degraded	% mass loss	
				Found	Calc.
2,6-DHAPDF-I	200 – 600 0C	First (Exo, b)	Loss of side chain (-CH2-NH-Ar-NH-,COCH3,2OH,-CH2) and partial degradation of aromatic nucleus	94.00	95.02

Table 2: Kinetic parameters for 2,6-DHAPDF-I Terpolymer resin

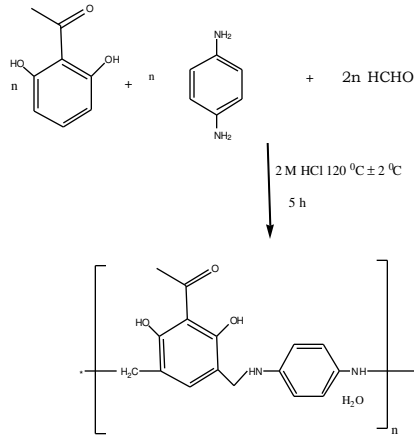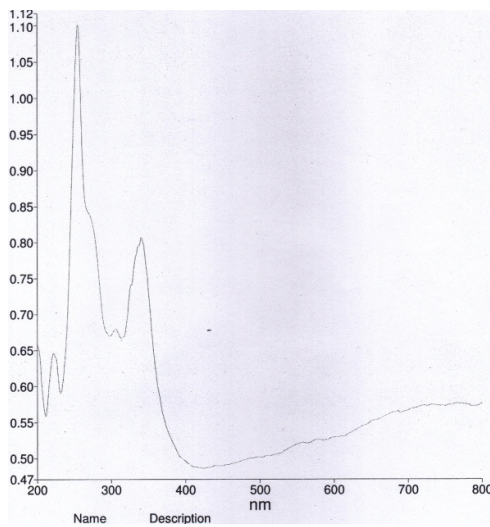| Terpolymer	Decompo Temp T (0C)	Half Decomp Temp (0C)	Activation Energy kJ/mole		Kinetic Parameters by FC				
			FC	SW	ΔS (J)	ΔF (kJ)	Z (S-1)	S* (J)	n
2,6-DHAPDF-I	2000C	400	28.24	31.00	-130.31	67.43	25.11	-20.76	0.96

Figure 1: Reaction for 2,6-DHAPDF-I Terpolymer Resin

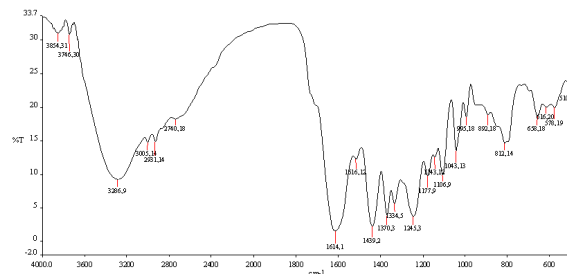

Figure 2: UV Visible Spectrum of 2,6DHAPDF Terpolymer resin

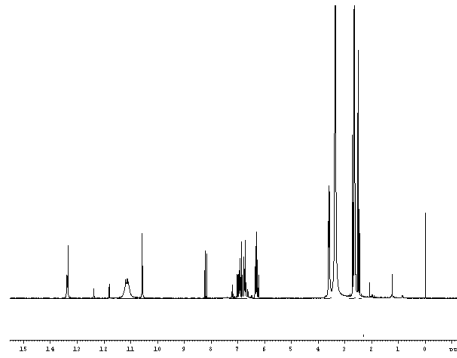**Figure 3:** IR-Spectral Data of 2,6-DHAPDF-I Terpolymer resin

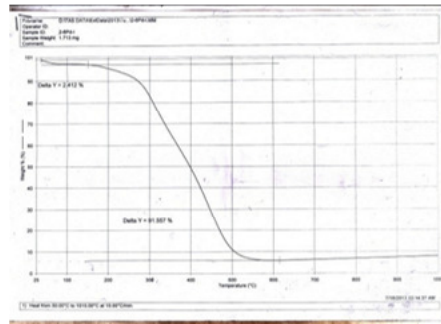**Figure 4:** ^{1}H NMR Spectra of 2,6-DHAPDF-ITerpolymer Resin

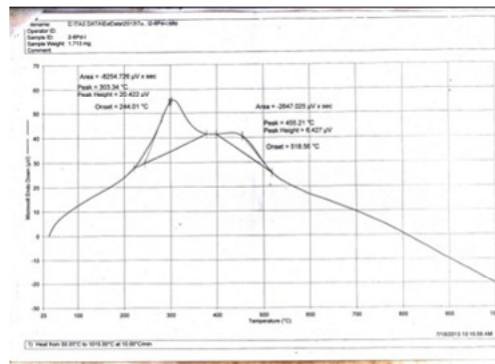**Figure 5**: TGA Graph for 2,6-DHAPDF-I

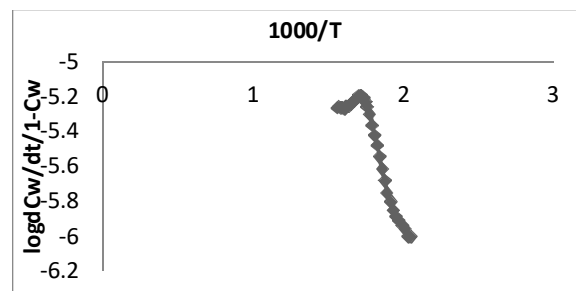**Figure 6:** DTA GRAPF FOR 2,6-DHAPDF-I

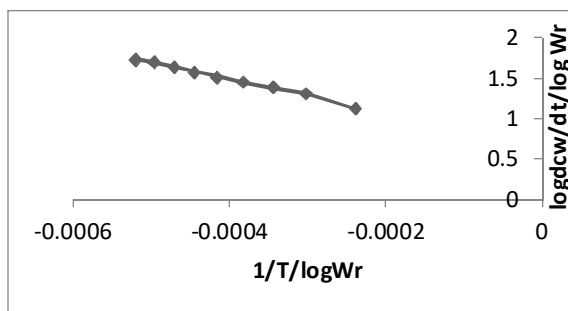**Figure 7:** Sharp-Wentworth plot of 2,6-DHAPDF-I Terpolymer Resin

Figure 8: Thermal Activation Energy Plot of 2,6-DHAPDF-I Terpolymer Resin
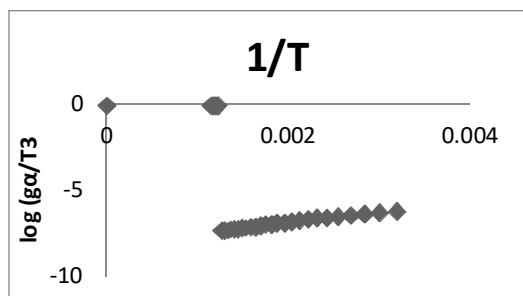

Figure 9: Freeman-Carroll plot of 2,6-DHAPDF-I Terpolymer Resin

References

1. Masram, D.T.; Kariya, K. P. and Bhave, N.S.; (2010). Electrical conductivity study of resin synthesized from salicylic acid, butylenediamine and formaldehydeArch. Apll. Sci. Res.2(2): 153-161

2. Shah, B. A.; Shah, A. V.; Bhandaria, B. N. and Bhatt, R. R.;(2008): Synthesis, Charecterization and Chelation Ion-Exchange Studies of a Resin CopolymerDerived from 8-Hydroxyquinoline-Formaldehyde-Catechol. J. Iran. Chem. Soc. 5(2): 252-261.

3. Fernandez B.; Arlas, D.; Rueda, L.; Stefani, P.M.; K.Mondragon, and A. Eceiza, (2007). Kinetic and thermodynamic studies of the formation of a polyurethane based on 1,6-hexamethylene diisocyanate and poly(carbonate-co-ester)diol, Thermochimica Acta, 459(2), 94-103.

4. Simionescu C.I, and A. Liga, (1977). Researches in the terpolymerization fieid.VIII. Theoretical structural study of the high conversion acrylonitrile-methacrylic acid- methyl methacrylate terpolymer, Revue Roumaine de Chimie, 22(1) 49-54.

5. Furukawa, J.; Iseda, Y.; Haga, K and Kataoka, N (1970). New information on the altering copolymerization of butadiene-1,3 with acrylonitrile, Journal polymer science part A-1, 8(5) 1147-1163,

6. Naguib, H. F.; Mokhtar, S.M.; Ali, R.O, and M. Z. Elsabee, (2003) Terpolymerization of ethyl methacrylate, N-phenylmaleimide, and itaconic acid. Journal Polymer Science A 41(20) 3180-3187,

7. Hirooka, M.; Yabuuchi, H.; Kawasumi, S. and Nakaguchi, K. (1973) Complex copolymerization of vinyl compounds with alkyaluminum halides. Journal Polymer Science A-1, 11(6) 1281-1306

8. Jadhav, M M.; Paliwal, L.J.; and Bhave, N.S.(2006)Resin II : thermal degradation studies of terpolymer resins derived from 2,2'-dihydroxybiphenyl, urea, and formaldehyde," Journal of Applied Polymer Science, 101(1) 227-232.

9. Paik P.and Kar, K.K.; (2008).Kinetics of thermal degradation and estimation of lifetime for polypropylene particles: effects of particle size. Polymer Degradation and Stability. 93(1) 24-35.

10. Vogel A. I., "Textbook of practical organic chemistry," Longman Scientific and Technical, U.K. **(1989).**

11. Freeman ES, Caroll B .(1958) The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate . J Phys Chem ;62: 394–397.

12. Sharp JB, Wentworth SA .(1969) Kinetic analysis of thermogravimetric data Anal Che; 41: 2060–2062.

13. Masram DT, Bhave NS, Kariya KP (2010). Kinetics study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde. E J Chem ;7:564–568.

14. Nielsen CA, Pierini P, Fuh S (1993). Thermal and thermo oxidativedegradation of poly (p-phenylene-cis-benzobisoxazole) (PBO):determination of kinetics and reaction products. J Fire Sci. ;11:156–71

15. Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR . Vogel's text book of practical organic chemistry. England: AddisonWesley Longman Ltd; 1998.

16. Ozawa T (1985) Critical investigation of methods for thermoanalytical data. J. Thermal Analysis and Calorimetry ;3(2):601-617.