Synthesis, Characterisation and Thermal degradation Studies of Resin -II derived from2,2'-Dihydroxybiphenyl, Phenylenediamineand Formaldehyde

Santosh P. Chakole¹, Priti Mishra² and W. B. Gurnule^{1*}

*¹Post Graduate Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur, 440024, India.

¹Department of Chemistry, D.L.S. P.G. College, Bilaspur-495004, CG India Email :wbgurnule@gmail.com chakole.santosh@gmail.com

Abstract-- 2,2'-DBPPHDF-II copolymer resin was prepared by polycondensation of the monomers 2,2'-dihydroxybiphenyl (DBP), phenylenediamine (PH) and formaldehyde (F) is in the molar ratio [2:1:3] in an acidic medium. Copolymer resin compositions and structure have been determined by elemental analysis,Number average molecular weight of copolymer resin was determined by conductometric titration in non-aqueous medium, Infrared spectra (FTIR), proton nuclear magnetic resonance spectra (¹H NMR) and the morphology of copolymer was studied by scanning electron microscopy (SEM). The studies have been further extended to nonisothermalthermogravimetric analysis (TGA) for determination of their mode of decomposition and relative thermal stability. Activation energy(Ea), order of reaction (n), and frequency factor (z) were calculated by Sharp-Wentworth and Freeman-Carroll methods. Activation energy calculated by Sharp Wentworth and Freeman-Carroll methods are in close agreement with each other.

Keywords-Synthesis, Polycondensation, thermal degradation, thermal stability, Freeman Carroll method, Sharp-Wentworth method.

I. INTRODUCTION

Study of thermal analysis comprises a group of techniques in which a physical property of substance is measured as a function of temperature when the substance is subjected to a controlled temperature program. Thermally stable terpolymers have recently become boon to polymer chemist due to their superior and high performance utility. Since the modern history of thermogravimetry, thermal degradation of polymers and the study of their kinetics have been at the centre of thermal analysis. Many researchers tried to improve the thermal stability at elevated temperature by changing the monomer composition in polymer synthesis.[1]

The thermal degradation study of terpolymer has become a subject of recent interest, being an important property, which primarily decides thermal stability and processability. A wide variety of thermally stable polymers have been synthesized and studied their thermogravimetric property and finds many applications such as ion-exchangers [2–5], semiconductors [6], high dielectric constant for energy storage capacitors [7], packaging, adhesives and coatings in electrical sensors, activators, catalysts and thermally stable materials [8–10]. Thermogravimetric analysis of terpolymer resins derived from 2,4-dihydroxyacetophenone, dithiooxamide, and formaldehyde by Rahangdale et al. [11], Michael et al. carried out thermal degradation of terpolymers synthesized from salicylic acid / 8-hydroxyquinoline and guanidine with formaldehyde [12, 13]. Phenolic resins are known for their wide applications in various areas because of their thermal stability, easy availability, cost effectiveness, and some of their excellent properties [14]. The thermal stability of terpolymers has been extensively studied by employing the method of thermogravimetric analysis (TGA) by several authors.

Thermo analytical and kinetic studies of terpolymer resins derived from 8hydroxyquinoline-5-sulphonicacid/p-cresol, oxamide/melamine with formaldehyde have been reported by Singru et al. [15-18]. 2-hydroxy, 4-metoxybezophenone, 1,5-diaminonapthalene, formaldehyde by Das [19]. 2,6-dihydroxyacetophenone, ethylenediamine and formaldehyde by Nilay and 8hydroxyquinoline-5-sulphonicacid, catechol, and formaldehyde by Mandavgade et al. [20] has been studied in detail. 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 being negligible.

Various studies on synthesis, characterization and thermogravimetric analysis of some new polymeric resins have been reported. Hence, in the present investigation, it has been planned to study the non isothermalthermogravimetric analysis of terpolymer derived from 2,2'dihydroxybiphenyl, phenylenediamine and formaldehyde which has not been reported so far in literature.

II. EXPERIMENTAL

Materials

2,2'-dihydroxybiphenyl and phenylenediamine used in the present investigation of analytical grade purity were purchased from Sigma Aldrich Chemicals. Formaldehyde (37%) was purchased from S.D. Fine Chemicals, India. All the used solvents like N,N-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, acetone, and diethyl ether were procured from Merck, India.

Synthesis of Copolymer

2,2'-DBPPHDF-II copolymer was prepared by condensation polymerisation of 2,2'dihydroxybiphenyl, phenylenediamine with formaldehyde in 2M medium of hydrochloric acid in the molar ratio 2:1:3 at temperature 120°C in an oil bath with occasional shaking, to ensure thorough mixing for about 4 hrs. The brown coloured resinous product was obtained. The product obtained was washed with hot distilled water and methanol to remove the excess of 2,2'-dihydroxybiphenylformaldehyde copolymer which might be present along with 2,2'-DBPPHDF copolymer.The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether. The brown colour resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 2,2'-DBPPHDF is shown in Fig. 1.



Fig. 1. Synthesisof 2,2'-DBPPHDF-II Copolymer Resin

Analytical and Physico-Chemical Studies

The elemental analysis was carried out on Elemental Vario EL III Carlo Erba 1108 elemental analyzer instrument. The electronic absorption spectra (UV-visible) of the copolymer in DMSO was recorded on double beam spectrophotometer in the range of 200-800 nm. Infrared spectra of copolymer were carried out in najol mull on Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pellets in the range of 4000-500 cm⁻¹. ¹H NMR spectrum was recorded on Bruker Advance –II 400 MHz NMR spectrophotometer using DMSO-d₆ as a solvent. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by a JEOL JSM-6380, an analytical scanning electronic microscope. The TGA of the copolymer has been carried out using Perkin Elmer diamond TGA/DTA analyzer. All the analytical and spectral studies for the newly synthesized copolymer were carried out at sophisticated analytical instruments facility SAIF, Cochin University, Cochin, India.

Thermal studies

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 conditions increase in temperature at linear rate. The thermo gravimetric analysis was performed in air atmosphere with heating rate at 10 $^{\circ}$ C min⁻¹ using 5-6 mg of samples in platinum crucible from temperature of 40 $^{\circ}$ C to 800 $^{\circ}$ C and thermogram is recorded for 2,2'-DBPPHDF- II. With the help of thermogravimetricdata, the thermal activation energies (Ea) and order of reaction (n) calculated. Also, the other thermodynamic parameters such

as entropy change (ΔS), apparent entropy change (S*) free energy change (ΔF) and frequency factor (Z) were determined.

Theoretical considerations

Thermogram was interpreted and analysed to obtain information about the percentage weight loss at different temperatures which gives information about sample composition, product formed after heating. Kinetic parameters have been determined using Sharp-Wentworth and Freeman-Carroll methods as follows

Sharp- Wentworth method Using the equation derived by Sharp and Wentworth [22],

 $LogdC/dT 1-C=log(A/\beta)- Ea 2.303R.1 TT$ (1)

where,

dC/dT = rate of fraction of weight with change in temperature

 β = linear heating rate dT/dt.

The graph of $\log dC/dT$ 1–C versus 1/T has been plotted. The graph is a straight line with activation energy (Ea) as slope and 'A' as intercept. The linear relationship confirms that the assumed order (n=1) is correct.

Freeman-Carroll method

The straight line equation derived by Freeman and Carroll [23], which is in the form of

 $\Delta \log f_0 (dW/dt) \Delta \log Wr = n - Ea 2.303 R\Delta (1/T) \Delta \log Wr \quad \dots \dots \dots \dots \dots (2)$

where,

dW/dt = rate of change of weight with time.

Wr = Wc - W

Wc = Weight loss at completation of reaction.

W = Fraction of weight loss at time t.

Ea= Energy of activation.

n = Order of reaction.

The plot between the terms $\Delta \log f_0 (dW / dt) \Delta \log Wr$ versus $\Delta (1 / T) \Delta \log Wr$ gives a straight line. The slope, Ea/2.303R, gives energy of activation (Ea) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (Z), apparent entropy change(S*) can also be calculated by further calculations.

III. RESULTS AND DISCUSSION

The newly synthesized 2,2'-DBPPHDF-II copolymer was found to be brown in colour. The copolymer is soluble in solvents such as dimethylformamide (DMF), Dimethylsulphoxide (DMSO), Tetrahydrofuran (THF) concentrated aq.NaOH and KOH, but insoluble in almost all organic and inorganic solvents.

Elemental Analysis

The 2,2'-DBPPHDF-II copolymer was analysed for the carbon, hydrogen and nitrogen content. The composition of copolymer obtained on the basis of elemental analysis data was found to be in good correlation which is presented in Table1. copolymer was analysed for the carbon, hydrogen and nitrogen content. The composition of copolymer obtained on the basis of elemental analysis data was found to be in good correlation which is presented in Table1.

Copolymer	% of C	% of H	% of N	% of O	Empirical	Empirical
resin	Observed	Observed	Observed	Observed	Formula of	Formula
	(cal.)	(cal.)	(cal.)	(cal.)	repeated	weight
					unit	
2,2'-	75.46	5.85	5.01	13.68	$C_{33}H_{28}N_2O_4$	516
DBPPHDF-	(76.74)	(5.43)	(5.43)	(12.40)		
II		()	()	()		

Table 1.	
Elemental analysis and empirical formula of	copolymer resi

The number average molecular weight (Mn)was determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required forneutralization of 100 gm of terpolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized.From the plot the first and final breaks were noted. The average degree of polymerization (DP) and hence the number average molecular weight (Mn) of the copolymer has been determined using the formula. This observation is in agreement with the trend observed by earlier workers [24].The conductometric titration curve as shown in Fig. 2and the result is shown in Table 2.

Total milliequivalents of base required for complete neutralization

DP =

Milliequivalents of base required for smallest interval

 $Mn = \overline{DP} \times M\overline{Olecular}$ weight of repeating unit



Fig.2. Conductometric titration curve of 2,2'- DBPPHDF-II Copolymer Resin

Wolceular weight determination of 2,2 -DBFF IID-II Copolymer							
Copolymer	First stage of	Final stage of	Degree of	Empirical	Number		
	neutralisation	neutralisation	polymerisation	formula	average molecular		
	Meq./100g sample	Meq./100g sample	DP —	weight			
				(n)	vmass		
	1	1					
2,2'-	392	1350	3.44	516	1775		
DBPPHDF-							
II							

Table 2.
Molecular weight determination of 2,2'-DBPPHD-II Copolymer

UV-visible spectrum

The UV-visible spectra of 2,2'- DBPPHDF-IIcopolymer resins are shown in Fig.3. UVvisible spectra of all the purified resins have been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min-1 and at a chart speed of 5 cm min-1. The perused of the UV-visible spectra of copolymers should almost similar nature. The spectra of these copolymersexhibit two absorption maxima in the region 248.50 and 282.50 nm. These observed positions of the absorption bands indicate the presence of hydroxy group, which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition, while the later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic shift i.e. Σ max higher values. This observation is in good agreement with the proposed most probable structures of these copolymer resins.



Fig.3. UV- Visible spectra curve of 2,2'- DBPPHDF-II Copolymer Resin

FT-IR Spectrum

The IR spectrum of terpolymer is shown in Fig.4. A broad band appearing in the region 3396.49cm^{-1} may be assigned to stretching vibrations of phenolic –OH groups. The band at 2925.04 cm⁻¹, and 1509.48 cm⁻¹, are assignable to –NH- stretching, bending and deformation out of plane respectively. The band at 1606.88 cm⁻¹ may be ascribed to an aromatic skeletal ring. The presence of methylene bridges (-CH₂-) in the polymeric chain may be assigned to the presence of a band at 1221.36 – 1019.83. and 820.89 cm⁻¹ [-CH₂- bending, wagging and rocking]. The bands obtained in the range 937 cm⁻¹, 1074.46 cm⁻¹ and 1123.45 cm⁻¹ confirms the 1,4 substituted aromatic ring. The 1.4 – substitution of the benzene ring is also confirmed by the presence of a band at 444.95 cm⁻¹ and 411.15 cm⁻¹ for a disubstituted benzene ring.



Fig.4: Infrared spectra of 2,2'-DBPPHDF-II Copolymer Resin

Observed band frequencies (cm ⁻¹)	Assignment	Expectedband frequencies(cm ⁻¹)
3396 (b, st)	-OHPhenolic,Intermolecular H- bonding	3750-3200
2925(s)	-NH,Stretching	3500-2800
1607(s)	Aromatic ring	1400-1680
1221(st)	-CH ₂ Stretching	1200-1350
1074(w)	1,3- substitution in benzene	800-1050
1509(s)	-CH ₂ bridge	1300-1500
445(w)	Ring substitution	400-700

Table. 3.FT-IR Data of 2,2'-DBPPHDF-II Copolymer Resin

¹H-NMR Spectrum

¹H NMR spectra of 2,2'-DBPPHDF-II are presented in Fig. 5 and NMR spectral data is shown in table 3. These spectra show a multiple signal (asymmetrical pattern) in the region 6.7 to 7.2(∂) ppm, which are due to aromatic protons. A doublet signal appearing in the region 8.1-8.4 (∂) ppm can be assigned to the proton of the phenolic –OH group involved in hydrogen bonding. Proton of aromatic amine Ar-NH₂ gives singlet at 4.55ppm. Methylenic proton of –NH–CH₂–linkage gives singlet at 3.7 and 2.5 ppm.A medium signal in the range of 3.7-4.0 (∂) ppm is attributed to the presence of –NH- bridging [25].



Fig. 5. ¹H NMR Spectra of 2,2'-DBPPHDF-II Copolymer Resin

Scanning Electron Microscopy(SEM)

Fig. 6 represents the scanning electron micrographs of 2,2'-DBPPHDF-II copolymer resin. The photographs of 2,2'-DBPPHDF-II copolymer exhibit sponge like structure derived from the aggregation of small granules. At lower magnification the resin shows spherulites in which the crystals are arranged smaller in surface area with more closely packed structures. This indicates the crystalline nature of the copolymer resin and this property shows the low ion exchange capacity for higher hydrated size metal ion. At different magnification the resins show more

amorphous character with less closed packed surface having deep pits. The amorphous character indicates that resin thus possesses higher exchange for metal ions. The morphology thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion-exchange capacity. The polymerization reaction proceeds by introducing amorphous character in the copolymer sample [26].



Fig. 6. Scanning Electron Microscopy of 2,2'-DBPPHDF-II Copolymer Resin Thermogravimetric Analysis

2,2'-DBPPHDF-II copolymer was subjected to thermogravimetric analysis and the data was used to assess the degradation pattern. Thermal degradation behaviour of synthesized copolymer has been incorporated in Table 4.and decomposition pattern is shown in Fig.7in temperature range from 40 to 850°C.Decomposition pattern of copolymer thermogram shows four decomposition steps in which the loss of water molecule (3.26% expected and 3.37% calculated) has been observed up to 150°C. first step decomposition step starts from 150 to 280°C which represents the degradation of phenolic -OH groups attached to aromatic nucleus (16.44% expected and 16.11% calculated). The Second decomposition step starts from 250 to 360°C, corresponding to 58.41% mass loss of aromatic nucleus against calculated 58.85%. The third decomposition step starts from 360 to 540°C which corresponds to loss of side chain of phenylenediamine. In fourth step 540-800°C complete phenylenediamine moiety (98.67% expected and 100% calculated). Consequently, no residue may be assigned after complete degradation.



Fig.7: Decomposition pattern of 2,2'-DBPPHDF-II copolymer.

Kinetics of Thermal Decomposition by the, Sharp and Wentworth, and Freeman-Carroll Methods.

The observed thermal stability of 2,2'-DBPPHDF-II copolymer terpolymer may be due to the stronger intermolecular hydrogen bonding present in polymer which may be attributed due to the presence of water of crystallization resulting in the resistance to higher temperature. By applying the thermogravimetric data to four thermal degradation kinetic methods, that is, the Sharp and Wentworth, and Freeman-Carroll methods, it shows four different degradation steps corresponding to loss of respective groups. The thermoanalytical data has been determined for different stages as given in Table 4. This kinetic analysis should be a starting point to obtain the useful information on the behaviour of sample. 1

Copolymer 2,2'-DBPPHDF-II						
Activation	Half	Entropy	Free	Frequency	Apparent	Order
energy	Decomposition	Change	Energy	factor Z	Entropy	of
	Temp.T*K	$\Delta S(J)$	Change	(S ⁻¹)	Change	reaction
F.C S.W			ΔF (kJ)		(S*)	(n)
16.13 18.1	685	-152.46	34.60	534	-22.97	0.9

Table 4: Kinetic Parameters of 2,2'-DBPPHDF-II copolymer resin

To obtain the relative thermal stability of terpolymer2,2'-DBPPHDF-II, the methods described by Sharp and Wentworth, and Freeman-Carroll were adopted. From the results, it is concluded that the values of kinetic parameters show good agreement with each other in Sharp and Wentworth and Freeman-Carroll's methods as shown in Table 4.

Fairly comparable results of kinetic parameters, namely entropy $change(\Delta S)$, energy of activation (Ea),order of reaction (n). frequency factor (z), apparent entropy (S*)are obtained for each degradation step obtained by Sharp and Wentworth and Freeman-Carroll methods are in good agreement with each other with slight variations between the results; it is concluded that the values of kinetic parameters depend on

kinetic methods used as well as degrading species at a particular step. Total calculations obtained from different kinetic methods demonstrated that the numerical value of kinetic parameters depends on the mathematical models used to analyse the experimental data and level of degradation. By using the above-mentioned techniques, variations in the results are obtained which represents versatility and great utility of thermal degradation of mathematical kinetics equations in thermogravimetry. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism.

From the thermogravimetric analysis, kinetic plots of the copolymer have been shown in Figures 8,9 and 10.



Fig.8: Sharp and Wentworth's plot of 2,2'-DBPPHDF-II copolymer.



Fig.9: Freeman-Carroll's plot of 2,2'-DBPPHDF-II copolymer for order of reaction.



Figure 10: Freeman-Carroll's plot of 2,2'-DBPPHDF-II copolymer for activation energy.

By using the above-mentioned methods, slight variations are obtained in between Sharp and Wentworth and Freeman-Carroll method which are found to be in good agreement with each other. From the point of view of chemical kinetics, 2,2'-DBPPHDF-II is thermally stable.

Low values of frequency factor revealed that decomposition reaction of terpolymer may be slow and no other possible reason can be given. However, in Freeman-Carroll, and Sharp and Wentworth's plots, all points did not fall on straight line, which indicates that the decomposition of terpolymer is not obeying first order of reaction perfectly [27-28].

IV. CONCLUSION

Synthesis of targeted copolymer (2,2'-DBPPHDF-II) has been confirmed which is supported by the results obtained by elemental analysis and spectral data. From the elemental analysis, UV visible, IR, and ¹H-NMR spectral studies, the proposed structure of the synthesized copolymer is confirmed. The values of kinetic parameter obtained from the Sharp and Wentworth and Freeman-Carroll methods are in good agreement with each other. Thermogram of copolymer resin shows four degradation steps and ethylenediamine molecule almost degrades completely up to 800°C. From the results obtained, the values of kinetic parameters are significantly controlled by the level of degradation and calculation methods used to analyse the experimental data.In TGA the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the kinetic parameters obtained from Freeman Carroll method are found to similar, indicating the common reactionmode. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism. Low values of collision frequency factor (Z) may be concluded that the decomposition reaction of 2,2'-dihydroxybiphenyl, phenylenediamine and formaldehyde copolymer can be classified as 'slow reaction'. The decomposition reaction was started at higher temperature, indicating a copolymer 2,2'-DBPPHDF-II is thermally stable at higher temperature.

Alochana Chakra Journal

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to Principal, Kamla Nehru Mahavidyalaya, Nagpur, India for cooperation and for providing necessary laboratory facilities and to the Director, STIC Analysis Cochin for carried out spectral analysis and thermal analysis.

REFRENCES

- [1] P. U. Belsare, A. B. Zade, P. P. Kalbende, M. S. Dhore,; J. Polym. Vol.10, pp.1-9, 2014.
- [2] W. B. Gurnule, P. K. Rahangdale, L.J.Paliwal, and R. B. Kharat, J. Appl. Polym. Sci. vol.89(3), pp.787-790, 2003.
- [3] V. D. Mane, N. J. Wahane, and W. B. Gurnule, ;J.Appl. Polym Sci. (111) 6, 3039-3049, 2009
- [4] M. V. Tarase, A. B. Zade, and W. B. Gurnule,; J. Appl. Polym. Sci., 108, (2), 738-746, 2008.
- [5] M. R Ahamed., R. Azarudeen, M. Karunakaran, T. Karikalan, A. Burkanudeen, Int. J. Chem. and Env. Engg, vol. 1(1), pp.7-12, 2010.
- [6] A. D. Kushwaha, A. B. Kalambe, V. V. Hiwase, and D. N. Urade, J. Chem. Pharma. Res., vol.4(2), pp.1111-1116, 2012
- [7] S. Dailey, W. J. Feast, R. J. Peace, I. C. Sage, S. Till, and E. L. Wood, J. Mater. Chem., vol.11(9), pp.2238-2243, 2001.
- [8] S. Pashaei, S. Siddaramaiah, M. M. Aval, and A. A. Syed,; Chem. Ind. and Chem. Engg. Quart., vol.17(2), pp.141-151, 2011.
- [9] W. B. Gurnule, S. P. Dhote, J. Chem. Pharm. Res., vol.5(12), pp.942-949, 2013.
- [10] M. Karunakaran, C. T. Vijayakumar, C. Magesh, and T. Amudha, Int. J. Engg. Sci. Tech., vol.3(1), pp.162-176, 2011.
- [11] V. R. Bisen, W. B. Gurnule, *Res. J. Bio. Chem. Sci*, vol.5(4),pp.1283-1297, 2014.
 [12] S. S. Rahangdale, A. B.Zade, and W. B. Gurnule, *Ultra Science*, vol.19, pp.213–218, 2007.
- [13] S. P. Dhote, W. B. Gurnule, J. Chem. Pharm. Res., vol.5(12), pp.942-949, 2013.
- [14] R.M. Zalloum, S.M. Mubarak, J. ApplPolym. Sci, vol.109, pp.3180-3184, 2008.
- [15] N.P.S. Chauhan.J. Ther. Anal.and Cal., vol.110 (3), pp.1377–1388, 2012.
- [16] W. B. Gurnule, P. K. Rahandale, L. J. Paliwal and R. B. Kharat, Reac. Funct. Polym, vol.55(3), pp.255-265, 2003.
- [17] M. M. Yeole, S. Shrivastava, W. B. Gurnule, Der PharmaChemica, vol.7(5), pp.124-129, 2015.
- [18] W. B. Gurnule, C. S. Makde, M. Ahmed, J. Env. Res. Develop., vol.7(3), pp.1183-1192, 2013.
- [19] S. Gharbi, J. Khiari, B. Jamoussi, J. Chem. Eng. Process Technol, vol.5(4), pp.1-7, 2014.
- [20] A. N. Gupta, V. V. Hiwas, A. B. Kalamble. Der Pharmachemica, vol.5(2), pp.105-112, 2013.
- [21] N. C. Das and W. B. Gurnule, Int. J. Curr. Engg. Sci. Res, vol.6 (1), pp.1414-1425, 2019.
- [22] S. K. Mandavgade, J. R. Dontulwar, and W. B. Gurnule, *Der PharmaChemica*, vol.4(4), pp.1695–1703, 2012.
 [23] J. B. Sharp, S. A Wentworth., Anal. Chem., vol.41(14), pp.2060-2062, 1969.
- [24] E. S. Freeman, B. J. Carroll, Phys. Chem., vol.62 (4), pp.394-397, 1958.
- [24] M.A. R. Ahmad, R. S Azarudeen, M.Karunakaran, A. R Burkanudeen, Iranian Polym. J., vol.19 (8122), pp.635-646, 2010.
- [25] M. M. Patel, M. A. Kapadia, G. P. Patel, J. D. Joshi, Iranian Polym. J., vol.16(62), pp.113-122, 2007.
- [26] S. Mane, S. Ponrathnam, , N. Chavan; Des. Monomers Polym, vol.18, pp723-733, 2015.
- [27] R.M. Zalloum, S.M. Mubarak, J. Appl. Polym.Sci., vol.109, pp.3180-3184, 2008.
- [28] N.P. S. Chauhan, J. Thermal Analysis and Calorimetry, vol.110(3), pp.1377–1388, 2012.