

Synthesis and Characterization of 2-Amino 6-Nitrobenzothiazole-Adipamide-Formaldehyde Copolymer

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Abstract: *The copolymer ANBAF-II was made via condensation of 2-amino 6-nitrobenzothiazole, adipamide and formaldehyde in the presence of 2M HCl as a catalyst at 126 °C in a 2:1:3 molar fraction of reactants. The structure of a newly synthesized copolymer has been elucidated and demonstrated using the concept of elemental evaluation and a variety of spectrum techniques, including UV-Visible, FT-IR, and ¹H NMR. The non-aqueous conductometric titration was used to determine the range of common molecular weight of the copolymer. The structure of the copolymer has been provided based on the idea of spectral and physicochemical evaluation.*

Keywords: Copolymer, condensation, spectral analysis, NMR spectra, Non-aqueous, Number average molecular weight.

I. INTRODUCTION

Functional polymers are used as simple inputs in generating substances along with plastic, rubber, fiber, paint, and adhesive because of their mechanical and technical homes [1]. The amendment affords the possibility to alternate and enhance the bodily and chemical homes of polymers within side the favored direction. For this reason, polymer amendment has end up one of the maximum essential subjects in lots of studies laboratories and industries [2]. Copolymer has been attracting plenty interest of polymer chemist because of thrilling advanced homes that may satisfy the call for of contemporary-day society [3]. Since remaining decades, emphasis has been given on synthesis of thermally solid polymeric resins with regard low manufacturing value and simplicity of manufacture. The thermal degradation examine of copolymer which more often than not comes to a decision the thermal balance, process ability and essential facts approximately its realistic applicability. A big wide variety of copolymers were synthesized and locate many packages along with adhesives, packaging, coating in electric sensors, catalyst, activators, thermal solid substances, ion-exchangers [4, 5], excessive dielectric regular for strength garage capacitors [6] and semiconductors [7]. The sizable have enough money has been made to enhance the exceptional of copolymer both with the aid of using advent of a whole lot of practical monomers or with the aid of using enhancing methods. The thermal balance of copolymer were studied with the aid of using the usage of the technique of thermo gravimetric analysis (TGA) with the aid of using numerous authors [8-15].

Thermal degradation of copolymer derived from 2-aminothiophenol, hexamethylenediamine with formaldehyde [16]. Synthesis and thermal degradation research of melamine formaldehyde resin has been stated through S. Ullah et al [17]. The thermal conduct of newly synthesized copolymer derived from salicylic acid and thiosemicarbazide has been studied through Kamalakar et al [18]. A. Gupta and coworkers studied the thermal degradation and kinetics of terpolymer resin derived from p-hydroxybenzaldehyde, succinic acid with ethylene glycol [19]. Thermogravimetric evaluation of terpolymer resin derived from salicylic acid, hexamethylenediamine with formaldehyde through Das et al [20], 8-hydroxyquinoline and formaldehyde through Rathod et al [21] and salicylic acid, diamionaphthalene with formaldehyde through Nandekar K. A. [22] had been stated. The observe of non-isothermal decomposition and kinetic evaluation of 2,4-dihydroxybenzoic acid, melamine-formaldehyde copolymer has been stated through Butoliya et al

[23]. The current research article deals with synthesis and characterization copolymer resin derived from 2-amino 6-nitrobenzothiazole, adipamide and formaldehyde which has not been studied so far in literature. The synthesized copolymer have been characterized by spectral and physicochemical methods.

II. MATERIALS AND METHODS

2.1 Materials

All the chemicals were AR grade and chemically pure grade. 2-amino 6-nitrobenzothiazole (Alpha Aesar, India), adipamide (HiMedia, Mumbai, India) and formaldehyde (S. D. Fine Chemicals, India) were procured from market. Double distilled water was used for all experiments.

2.2 Synthesis of ANBAF-II Copolymer

The copolymer resin become synthesized by way of refluxing mixture of 2-amino 6-nitrobenzothiazole (0.2 mol), adipamide (0.1 mol) and formaldehyde (0.3 mol) in the presence of 2M, 200 ml HCl as a catalyst at 125.6 ± 2 °C for approximately 5h in an oil tub with occasional shaking. The separated brown coloration strong merchandise had been washed with warm water to do away with the unreacted monomers. The air dried product was extracted with diethyl ether to remove the two-amino 6-nitrobenzothiazole-formaldehyde copolymer along with the 2-amino 6-nitrobenzothiazole. It became further purified with the aid of dissolving in 8% NaOH after which filtered. The copolymer became then reprecipitated with the aid of dropwise addition of 1:1 (v/v) con HCl/water with regular stirring and filtered. The procedure of reprecipitation become repeated twice. The copolymer pattern as a result acquired turned into filtered, washed several instances with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the copolymer resin was found to be 83%. The reaction and suggested shape of ANBAF-II copolymer has been depicted in Fig. 1.

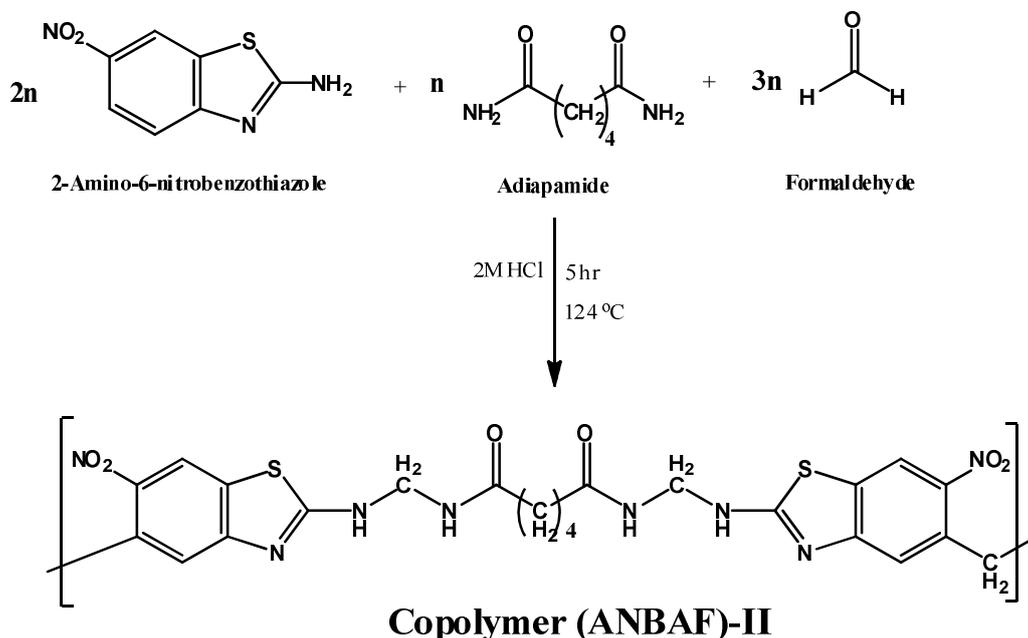


Figure 1: Synthesis of ANBAF-II copolymer

2.3 Analytical and Physico-chemical Studies

The elemental analysis of ANBAF-II copolymer resin was recorded on Elemental Vario EL III Carlo Erba 1108 elemental analyzer device. The UV-Visible spectra of the copolymer become carried out at room temperature in DMF on double beam spectrophotometer outfitted with computerized pen chart recorder inside the range of 200 nm – 850 nm. Infrared spectra of copolymer has been scanned in najol mull on Perkin-Elmer-Spectrum RX-I, FT-IR Spectrophotometer in KBr pellets within the variety of $4000-500$ cm^{-1} . The proton NMR spectrum of copolymer turned



4.2 UV-Visible Spectra

The UV-Visible spectra of ANBAF-II copolymer resin is presented in Fig. 3. UV-visible spectra of copolymer sample has been recorded in natural DMF in the vicinity 200–800 nm. The spectrum well-known shows absorption maxima inside the location 280 nm and 320 nm. These observed function of absorption band imply the presence of carbonyl group (ketonic) having a carbon-oxygen double bond that's in conjugation with aromatic nucleus. The appearance of former band (extra intense) can be accounted for $\pi \rightarrow \pi^*$ transition at the same time as the latter band (less extreme) may be due to $n \rightarrow \pi^*$ digital transition. The shift from the basic cost (viz. 240 nm and 310 nm respectively) can be due to conjugation effect and presence of nitro group (auxochrome) is chargeable for hyperchromic impact.

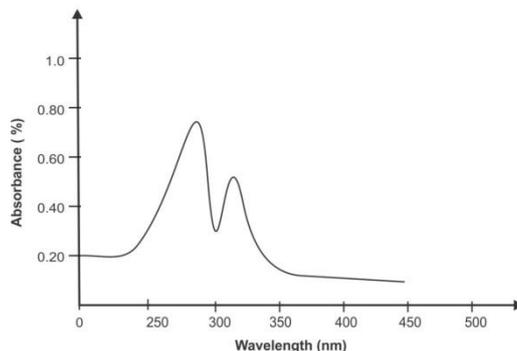


Figure 3: UV-visible spectra of ANBAF-II copolymer resin

4.3 FT-IR Spectra

Figure 4 shows the FTIR spectra of the ANBAF-II copolymer, with spectral data listed in Table 2. The vibration frequency is calculated using information from the literature. The stretching vibration of the -NH group may be assigned to a broad and strong band that appeared in the region 3290 cm^{-1} . At 2970 cm^{-1} , the presence of nitro results in a prominent and strong peak. The -NH- in the adipamide moiety could explain the sharp and faint band at 2939 cm^{-1} . The stretching vibration of the Ar-CO- group may be responsible for the strong band at 1628 cm^{-1} . The existence of the $>\text{C}=\text{C}$ (aromatic) group is shown by a sharp band at 1482 cm^{-1} . The existence of a crisp and strong band at 1373 cm^{-1} suggests the presence of -CH₂- methylene bridge in the copolymer chain. The presence of 1, 2, 3, 4 and 5-pentasubstituted aromatic ring is recognized from weak band appearing in the region $905\text{-}860\text{ cm}^{-1}$ [27].

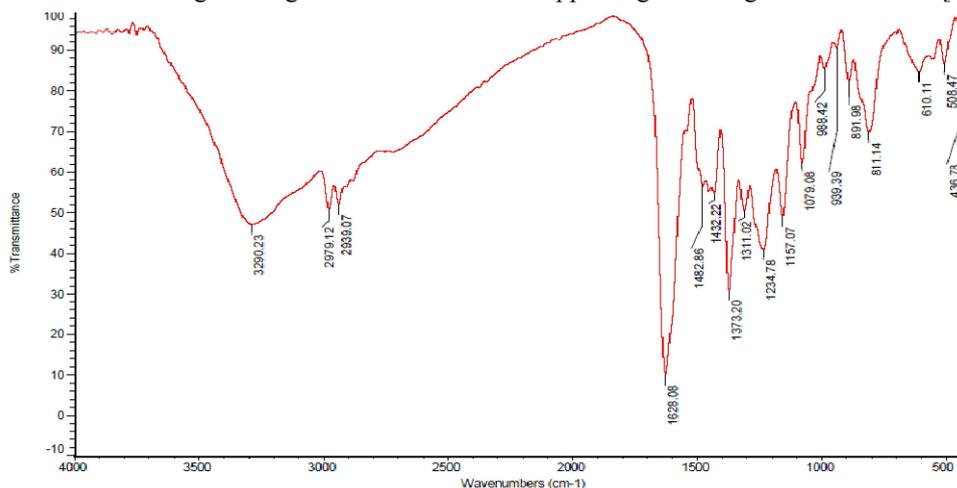


Figure 4. FT-IR Spectra of ANBAF copolymer resin

Table 2: FT-IR data of ANBAF copolymer

Observed band frequencies (cm ⁻¹)	Assignment	Expected band frequencies (cm ⁻¹)
3290 (b,st)	-NH group	
2979(sh, St)	-CH ₂ ,-CH ₃ stretching	3500-2800
2939(sh, w)	-NH- moiety in adipamide	3450- 2795
1447(Sh)	Aromatic ring	1445-1485
1344(sh,st)	-CH ₂ - bridge	1380-1350
1628(sh, st)	Ar-CO- group	1670-1630
891(m)	1,2,3,4,5-substitution	905-860

b=broad, st= strong, sh= sharp, w= weak, m=medium

4.4 H NMR Spectra

Figure 5 shows the ¹H NMR spectra of the ANBAF-II copolymer, with spectral data included in Table 3. Because each of them has a set of protons with a different proton environment, the spectrum exhibits a varied pattern of peaks. Due to aromatic proton, the weak multiplicity signals (unsymmetrical pattern) in the range of 7.1 ppm (Ar-H). Tiazole proton is responsible for a large singlet signal at 6.4 ppm. The amido proton Ar-CH₂-NH- of the copolymer chain may be responsible for the medium triplet signal at 7.6 ppm. Doublets signal in the area of 2.6 ppm can be used to identify the proton of the methylene bridge Ar-CH₂-NH-. The presence of quartet peaks in the 3.0 ppm range indicates that methylene proton is present [28].

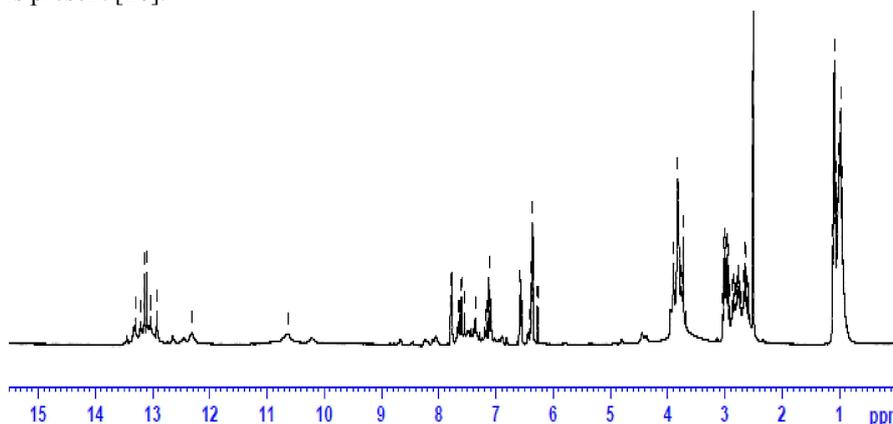


Figure 5: ¹H-NMR Spectra of ANBAF copolymer resin

Table 3: ¹H-NMR spectra of ANBAF-II copolymer

Observed shift δ (ppm)	Nature of proton assigned	Expected chemical shift δ (ppm)
6.4 s	Proton of NH group	8.0 to 12.0
7.1 m	Aromatic proton (Ar-H)	6.2 to 8.5
7.6 t	Proton of -NH bridge	5.0 to 8.0
2.6 d	Proton of Ar-CH ₂ -N moiety	2.0 to 3.0

3.0 q	Methylene proton of Ar-CO-1.8 to 4.5
CH ₂ -	

S= singlet, d= doublet, t=triplet, q= quartet, m= multiplets

4.5 Scanning Electron Microscopy

The surface features of ANBAF-II copolymer resin became studied by means of scanning electron micrograph at exclusive magnification which is presented in Fig. 6. It offers statistics approximately surface topography and defects inside the structure. The investigated copolymer appeared to be darkish brown in shade. At decrease magnification it suggests spherules wherein the crystals are organized extra closely in smaller surface region. It suggests the crystalline nature of resin and this belongings exhibits low ion trade ability for better hydrated length metallic ion. At higher magnification it indicates greater amorphous properties with much less close packed surface having deep pits. The amorphous nature of the resin shows better ion trade capability for metallic ion. Thus resin is crystalline as well as amorphous or transition among crystalline and amorphous, showing much less or more exact ion alternate ability [29].

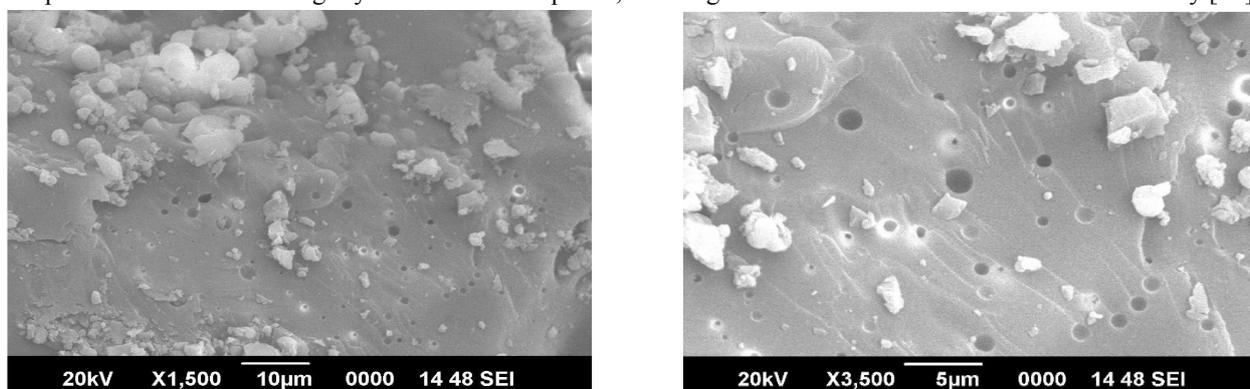


Figure 6. SEM Microgram of ANBAF copolymer

V. CONCLUSION

Condensation polymerization was used to make ANBAF-II copolymer from 2-amino 6-nitrobenzothiazole, adipamide, and formaldehyde in the presence of an acid catalyst. The chemical analysis, FT-IR, and ¹H NMR spectral investigations all validated the structure of the produced copolymer. The copolymer's average molecular weight was discovered to be 6846.

REFERENCES

- [1]. JA. Arenzano, JM. del Campo, JO. Virues, et al. Theoretical study of the hydrogen bonding interaction between Levodopa and a new functionalized pillared coordination polymer designed as a carrier system, *J. Mol. Struct.* 1083 (2015) 106–110.
- [2]. K. Demirelli, M. Coskun, I. Erol, Copolymerization and monomer reactivity ratios of 2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate with acrylonitrile, *Eur. Polym. J.* 36 (2000) 83-88.
- [3]. S. K. Kapse, V.V. Hiwase, A. B. Kalambe and J. D. Kene, Comparative thermokinetics study of terpolymericresins derived from p-hydroxyacetophenone, resorcinol and phenol, *Res. J. Chem. Sci.*, 4(2), (2014), 81-86.
- [4]. S.Pashaei, S.Sddaramaiah, M. M. Avval and A. A. Syed, Thermal degradation kinetics of nylon-6/gf/crysnano nanoclay nanocomposites by TGA, *Chemical Industry and Chemical Engineering Quaterly*, 17(20), (2011), 141-151.
- [5]. G.E.Zaikov, *Degradation and Stabilization of Polymers, Theory and Practice*, Nova Science Publishers, New Delhi, India, (1995)

- [6]. W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal and R. B. Kharat, Chelation ion-exchange properties of copolymer resin derived from 4-hydroxyacetophenone, oxamide and formaldehyde, *J. Appl. Polym. Sci.*, 89(3), (2003), 787-790.
- [7]. A. D. Kushwaha, A. B. Kalambe, V. V. Hiwase and D. N. Urade, Structural and antibacterial study of resin-II derived from p-nitrophenol, resorcinol and formaldehyde, *Journal of Chemical and Pharmaceutical Research*, 4(2), (2012), 111-116.
- [8]. Gurnule W. B., Butoliya S. S., Isoconventional and Thermal Methods of Kinetic Analysis 2,4-Dihydroxybenzophenone Copolymer Resin, *Journal of Applied Polymer Science*, Vol 122 2181-2188. (2011).
- [9]. W. Hackenberger, R. Alberta, W. Paul, D. Jeong and Q. Zhang, High dielectric constant terpolymers for energy storage capacitors, in *Proceedings of the 25th Symposium for Passive Components*, Palm Springs (2005), 239-243.
- [10]. W. B. Gurnule and V. R. Dhote, Kinetics of thermal decomposition of copolymer resin-II derived from 4-hydroxybenzaldehyde phenyl hydrazine and formaldehyde, *RJPBCS*, 5(4), (2014), 1283-1297
- [11]. C. Liu, J. Yu, X. Sun, J. Zhang and J. He, Thermal degradation studies of cyclic olefin copolymers, *Polymer Degradation and Stability*, 81, (2003), 197-205.
- [12]. Jyostna V. Khobragade, Mudrika Ahamed and W. B. Gurnule, Synthesis and Characterization of Copolymer Resin derived from phthalic acid and Melamine, *Rasayan J. Chem.*, Vol. 7(4), 413-419, (2014).
- [13]. M. E. S. R. Silva, E. R. Dutra, V. Mano and J. C. Machado, Preparation and thermal study of polymers derived from acrylamide, *Polymer Degradation and Stability*, 67, (2000), 491-495.
- [14]. S. S. Rahangdale, A. B. Zade and W. B. Gurnule, Thermal degradation studies of terpolymer derived from 2, 4-dihydroxyacetophenone, dithiooxamide and formaldehyde, *Ultra Science*, 19, (2007), 213-218.
- [15]. Z. P. Zhao, Q. Guo, X. Li, J. L. Sun and Z. J. Nie, Synthesis and thermal degradation, characterization of novel poly (phosphazene aryl amide), *eXPRESS Polymer Letters*, 6(4), (2001), 308-317.
- [16]. S. K. Mandavgade, J. R. Dontulwar, and W. B. Gurnule, Thermal degradation study of new polymer derived from 8-hydroxyquinoline 5-sulphonic acid and catechol, *Der PharmaChemica*, 4(4), (2012) 1695-1703.
- [17]. M. V. Tarase, A. B. Zade and W. B. Gurnule, Kinetics of thermal degradation studies of some new terpolymers derived from 2, 4-dihydroxypropiophenone, oxamide, and formaldehyde, *Journal of Applied Polymer Science*, 116(2), (2010), 619-627.
- [18]. W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, Synthesis, characterization and ion-exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resins, *Rect. Func. Polym.* 55 (3), 255-265, 2003.
- [19]. S. Ullah, M. A. Bustam, M. Nadeem, M. Y. Naz, W. L. Tan and A. M. Shariff, Synthesis and thermal degradation studies of melamine formaldehyde resins, *The Scientific World Journal*, Article ID 940502, (2014), 1-6.
- [20]. K. A. Nandekar, J. R. Dontulwar and W. B. Gurnule, Thermal behavior of newly synthesized copolymer derived from salicylic acid and thiosemicarbazide, *Der Pharma Chemica*, 4(4), (2012), 1644-1652.
- [21]. A. N. Gupta, V. V. Hiwase and A. V. Kalambe, Thermal degradation and kinetic study of terpolymer resin-II derived from p-hydroxybenzaldehyde, succinic acid and ethylene glycol, *Der Pharmacia Lettre*, 5 (2), (2013), 105-112.
- [22]. W. B. Gurnule and N. C. Das, Kinetic Study of Non-Isothermal Decomposition of Copolymer Resin Derived from 2, 4-Dihydroxypropiophenone, 1, 5-Diaminonaphthalene and Formaldehyde, *Materials Today: Proceedings* 15, 611-619, (2019).
- [23]. Y. U. Rathod, S. B. Zanje and W. B. Gurnule, Hydroxyquinoline copolymers synthesis, characterization and thermal degradation studies, *Journal of Physics: Conference Series*, 1913, 1-8 (2021)
- [24]. K. A. Nandekar and W. B. Gurnule, Synthesis and antimicrobial study of copolymer resins derived from p-hydroxybenzoic acid, semicarbazide and formaldehyde, *Journal of Physics: Conference Series*, 1913, 1-8 (2021).

- [25]. S. S. Butoliya, W. B. Gurnule, and A. B. Zade, Study of non-isothermal decomposition and kinetic analysis of 2,4-dihydroxybenzoic acid-melamine-formaldehyde copolymer, *E-Journal of Chemistry*, 7(3), (2010), 1101- 1107.
- [26]. W. B. Gurnule and Y. U. Rathod, Synthesis, Characterization and Thermal Behaviour Studies of Terpolymer Resin Derived from 8-Hydroxyquinoline-5-Sulphonic Acid and Anthranilic Acid, *Current Appl. Polym. Sci.*, 4, 47-54 (2021).
- [27]. M. M. Yeole, S. Shrivastava and W. B. Gurnule, Synthesis and characterization of copolymer resin derived from 4-methyl acetophenone, phenyl hydrazine and formaldehyde, *Der Pharma Chemica*, 7(5), (2015), 124-129.
- [28]. D. B. Patle and W. B. Gurnule, An eco-friendly synthesis, characterization, morphology and ion exchange properties of terpolymer resin derived from p-hydroxybenzaldehyde, *Arabian Journal of Chemistry*, (2011), 1-11
- [29]. W.B. Gurnule, C.S. Makde and M. Ahmed, Synthesis, characterization, morphology, thermal electrical and ion exchange properties of a copolymer resin, *J. Environ. Res. Develop.*, 7(3), (2013), 1183-1192.
- [30]. W. B. Gurnule and S.P. Dhote, Synthesis, characterization and thermal degradation studies of copolymer resin derived from 4-hydroxybenzophenone, melamine and formaldehyde, *J. Chem. Pharm. Res.*, 5(12), (2013) 942-949.
- [31]. R.N. Singru, A.B. Zade and W.B. Gurnule, Thermoanalytical study and kinetics of new 8-hydroxyquinoline-5-sulphonic acid-oxamide-formaldehyde copolymer resin, *E-Journal of Chemistry*, 6(S1), (2009), 171-182.