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Synthesis, Characterization and Morphology of Organic Copolymer Resin-III Resulting from 1,5-Diaminonaphthalene, 2,4-Dihydroxypropiophenone and Formaldehyde

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Abstract: *The copolymer 2,4-DHP-1,5-DANF-III has been synthesized from 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene with formaldehyde by the polycondensation method in the presence of 2M hydrochloric acid as a catalyst with 3:1:5 molar proportion of reactants. The copolymer has been characterized by various physico-chemical and spectral techniques such as elemental analysis, UV-Visible, FT-IR, ^{1}H-NMR and non-aqueous conductometric titration. Scanning electron microscopy (SEM) has been used to establish the surface morphology. The copolymer has been found to becrystalline as well as amorphous or transition between crystalline and amorphous.*

Keywords: Copolymer, Synthesis, Characterization, Morphology, Crystalline, Amorphous

I. INTRODUCTION

The synthesized copolymer showing versatile applications and properties which attracted the attention of scientist and introduces the innovations in polymer science. Copolymers have been changing our life for decades with many applications in the field including waste water treatment, ion-exchanger, medicine, engineering, agriculture, and semiconductor because of their high thermal stability, heat and chemical resistance. Thermogravi metric analysis has been widely used to investigate the decomposition characteristics of polymeric matter. The degradation of polymer under air or inert atmosphere at increasing temperature provides useful information about the nature of the species produced [1-5].

Electrical conductivity study of thermally stable newly synthesized copolymer has reported by Niley and coworker [6]. Gabal et al. have reported the synthesis, characterization and electrical conductivity of polyaniline-$Mn_{0.8}Zn_{0.2}Fe_2O_4$nano-composites [7]. Gupta has studied the electrical conductance behaviour of copolymer resin-II derived from p-hydroxybenzaldehyde, urea and ethylene glycol [8]. Chinchamalatpure and coworker have reported the electrical conductivity of some copolymers and its polychelates [9].Gurnule and coworkers studied the synthesis, characterization and thermal degradation study of copolymer derived from salicylaldehyde, melamine and formaldehyde [10]. Thermal degradation and electrical conductivity measurement of resin derived from salicylic acid, hexamethylenediamine and formaldehyde has been studied by DhanrajMasram et al. [11]. Terpolymer 8-hydroxyquinoline,formaldehyde with pyrogallol have been reported by SoumayaGharbi et al. [12]. Electrical conductivity of salicylidene - anthranilic acid - schiff base formaldehyde resin (R-AASA) was reported by Abbas and coworker [13]. The present investigation deals with study of synthesis and characterization of 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene with formaldehyde copolymer which has not been reported so far in literature.

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II. Materials and Methods

All the chemicals used were of AR grade. The 1,5-diaminonaphthalene (Himedia, India)2,4-dihydroxy-propiophenone(Alpha Aesar), and formaldehyde (S.D. Fine Chemicals) were procured from market. The solvents like Dimethylformamide(DMF), dimethylsulphoxide(DMSO), tetrahydrofuran(THF), acetone and dimethyl ether were purchased from Merck, India.

2.1 Synthesis of 2,4-DHP-1,5-DANF-III Copolymer

The copolymer2,4-DHP-1,5-DANF-III was synthesized by condensing 2,4-dihydroxypropiophenone and 1,5-diaminonaphthalene with formaldehyde in the presence of 2M HCL as a catalyst in 3:1:5 molar proportion of reactants in an oil bath for about 5hat temperature 126 $\pm$ 2^0C. The brown color product was obtained and washed with hot waterseveral times. The product obtained was extracted with diethyl ether to remove 2,4-dihydroxypropiophenone formaldehyde copolymer which might be present along with 2,4-DHP-1,5-DANF-III copolymer. It was further purified by dissolving in 8% NaOH and then filtered. The copolymer was then reprecipitate by drop wise addition of 1:1 con. hydrochloric acid and water with rapid stirring to avoid the lumping formation. The purified sample was dried, powdered and kept in vacuum desiccators. The yield of the resin was found to be 78 %. The reaction of above synthesis has been depicted in Figure-1.

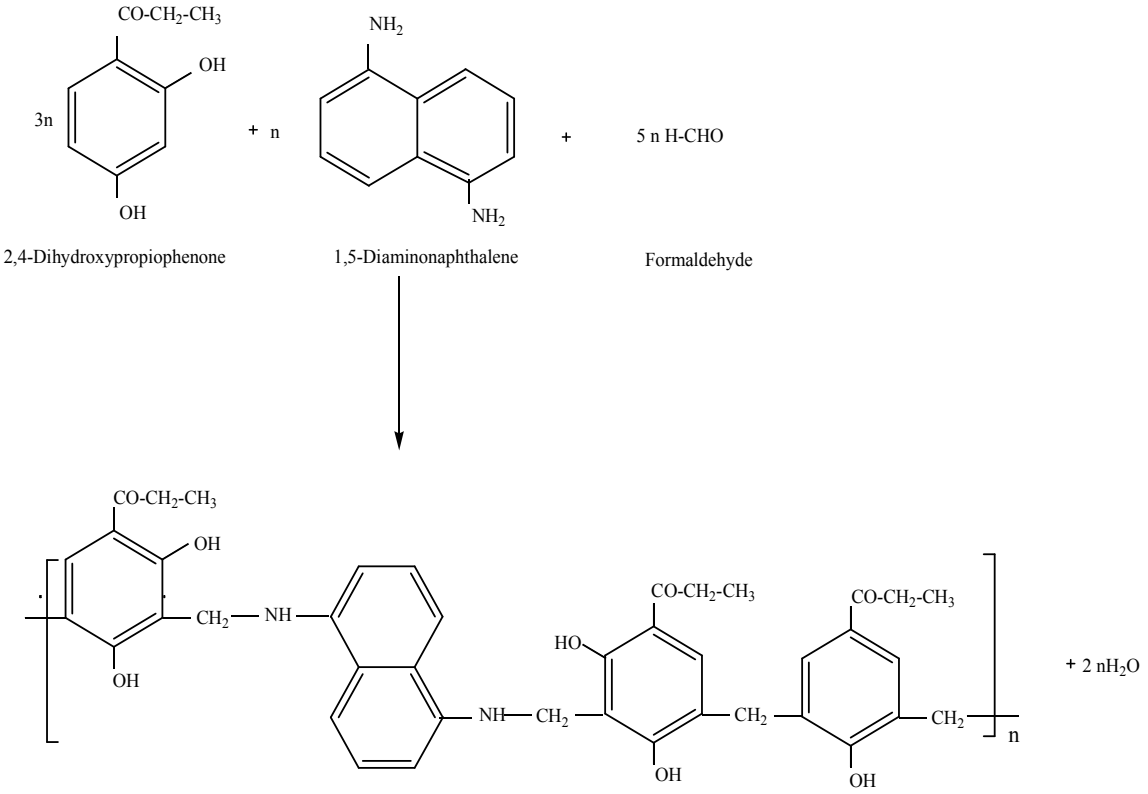

Figure 1: Synthesis of 2,4-DHP-1,5-DANF-III copolymer resin

2.2 Analytical and Physico-Chemical Studies

The elemental analysis of the copolymer resin 2, 4-DHP-1,5-DANF-IIIwas carried out on Elemental Vario EL III Carlo Erba 1108 elemental analyzer instrument. The UV-Visible spectra was recorded at room temperature in dimethylsulphoxide in the range of 190 nm - 850 nm on double beam spectrophotometer fitted with automatic pen chart recorder. FT-IRspectra has been carried out on Perkin-Elmer-Spectrum RX-I, FT-IR Spectrophotometer in the range of 4000-500 cm^{-1} in KBr pellets. The ^{1}H- NMR spectrum of the resin was recorded using DMSO-d_6 as a solvent on

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Bruker Advance -II 400 MHz NMR spectrophotometer. For the synthesized copolymer resin,all the analytical and spectral studies were recorded at Sophisticated Analytical Instruments facility, STIC, Cochin University, Cochin, India.

II. Results and Discussion

The synthesized copolymer resin was found to be brown color. The copolymer is soluble in solvent such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and tetrahydrofuran(THF) but insoluble in almost all other inorganic and organic solvents. The yield of the copolymer is 81%.

3.1 Elemental Analysis

The copolymer 2,4-DHP-1,5-DANF-III has been analyzed for carbon, hydrogen and nitrogen contents. The empirical formula and empirical formula weight has been evaluated based on the analytical data and is presented in the Table-1.The values of percentage of elements determined are in good agreement with calculated values.

Table 1: Elemental analysis and empirical formula of copolymer resin

Copolymer resins	% of Carbon observed calculated	% of Hydrogen observed calculated	% of Nitrogen observed calculated	Empirical formula of repeat unit	Empirical formula of repeat unit
2,4-DHP-1,5-DANF-III	68.32 69.88	6.20 5.68	4.32 3.97	$C_{41}H_{40}N_2O_9$	704

3.2 Number Average Molecular Weights ($\overline{Mn}$) by Non-aqueous Conductometric Titration

The number average molecular weights ($\overline{Mn}$)of the resin has been evaluated by conductometric titration method in non-aqueous medium using alcoholic 0.05M KOH as a titrant. The specific conductance was plotted against milliequivalents of alcoholic KOH required for neutralization of 100g of copolymer. It has found that there were many breaks in the plot. The first break at 280 milliequivalents of base and the last break at 1288milliequivalent of base were noted (Fig. 2). The calculation of $\overline{Mn}$by this method is based on the following considerations, (1) The first break corresponds to neutralization of one phenolic hydroxyl group of each repeat unit; (2) The break in the plot beyond which a continuous increase is observed represents the stage at which all phenolic hydroxyl group of the repeating units are neutralized [16]. On the basis of the average degree of polymerization ($\overline{DP}$), the number average molecular weight has been determined by the following relations

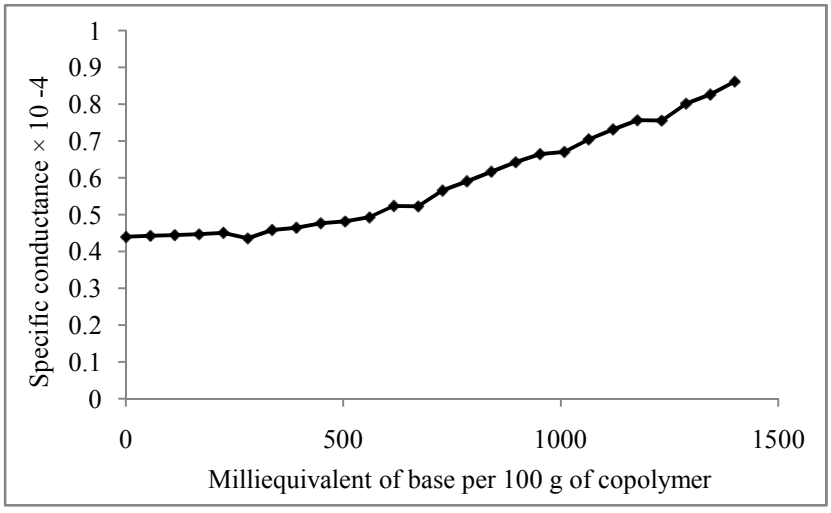

Figure 2: Conductometric titration curve of 2,4-DHP-1,5-DANF-III copolymer resin

$$(\overline{DP}) = \frac{\text{Total milliequivalents of base for complet neutralization}}{\text{Milliequivalents of base required for smaller intervals}}$$

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$\overline{Mn}$= $\overline{DP}$x Repeat unit weight

The number average molecular weight ($\overline{Mn}$) has been found to be 3238 and average value of $\overline{DP}$ is 5.0

3.3 UV-Visible Spectra

The UV spectra of the copolymer 2,4-DHP-1,5-DANF-III is shown in Figure-3. The spectrum of resin has been scanned in pure DMSO in the region 190-800nm. The spectra exhibits two characteristics absorption maxima in the region 270 nm and 320nm. The observed position of absorption bands indicate the presence of carbonyl group (>C=O) having carbon-oxygen double bond which is in conjugation with aromatic nucleus. The appearance of more intense can be accounted for π→π* transition while the less intense band may be due to n→π* electronic transition. The shift from basic value (viz. 240nm and 310nm respectively) may be due to combined effect of conjugation and phenolic hydroxyl group (auxochrome)[14].

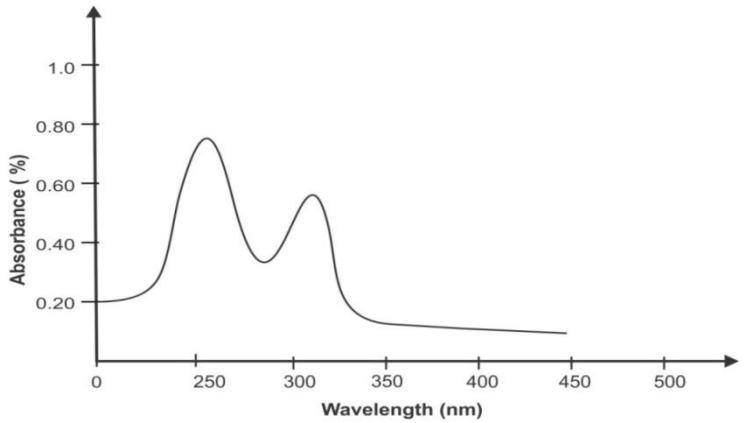

Figure 3: UV-visible spectra of2,4-DHP-1,5-DANF-III copolymer resin

3.4 FT-IR Spectra

The FT-IR spectra of 2,4-DHP-1,5-DANF-III copolymer is shown in Figure-4. The band appeared at 3243 cm^{-1}maybe due to the stretching vibration of phenolic hydroxyl group exhibiting intramolecular hydrogen bonding. The sharp and strong band observed at 1626 cm^{-1}may be on account of stretching vibration of carbonyl group (Ar-COgroup). The medium band in the region 2978 cm^{-1}suggest the –NH- group in pyridine moiety. The presence of methylene vibration has been indicated by the band at 2938cm^{-1}. A weak band observed at 1458 cm^{-1}indicates the presence of>C=C< (aromatic) group. The sharp and strong band appeared at 1373 cm^{-1}, suggested the presence of –CH_2-methylene bridge in copolymer chain[15].

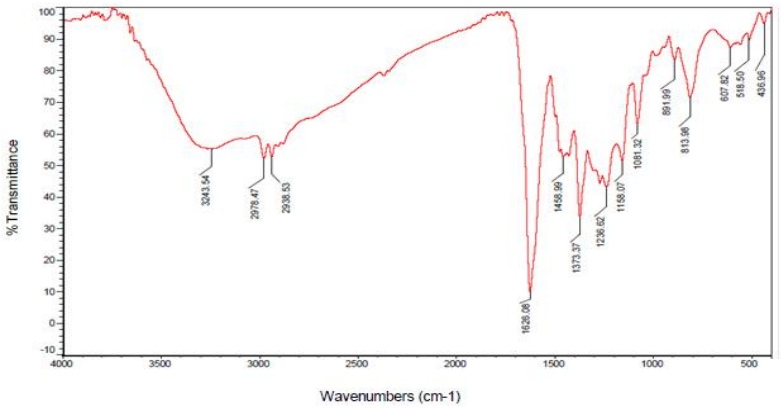

Figure 4: FT-IR-Spectra of 2,4-DHP-1,5-DANF-III copolymer resin

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3.5 ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of 2,4-DHP-1,5-DANF-III is shown in Figure-5.NMR spectra shows weak multiplicity signal at 6.3 (δ) ppm which that is due to aromatic protons (Ar-H). A singlet signal appeared in the region 7.1(δ) ppm is due to the phenolic -OH proton in intramolecular hydrogen bonding. The methyl proton of Ar-CO-CH_2-CH_3 is recognized by the triplet signal in the region 1.1(δ) ppm. The quartet signal appeared at 2.9 (δ) ppm reveals the presence of methylenic proton of Ar-CO-CH_2-CH_3 group. The proton of methylenicbridgeAr-CH_2-NH- may be identified as doublet signal observed at 2.5 (δ)ppm. The triplet signal in the region 7.6(δ) ppm may be due to proton of –NH- bridge (amido) of copolymer chain [16-17].

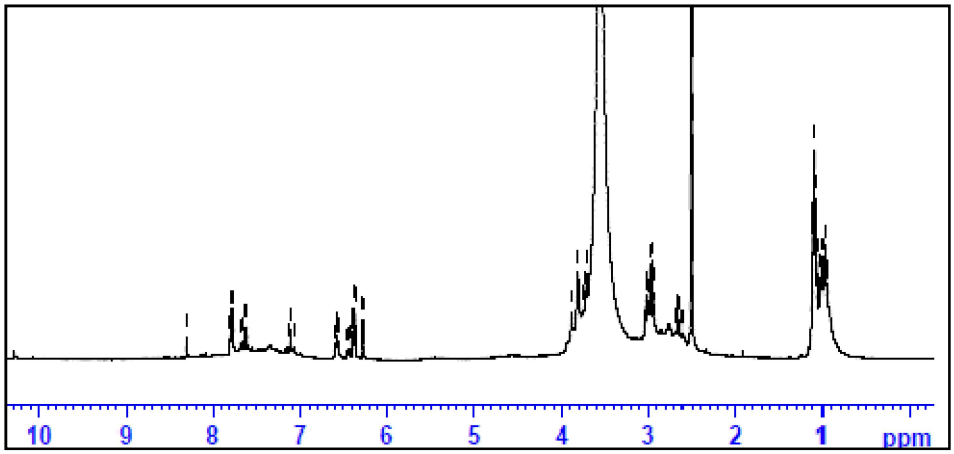

Figure 5: H^{1}-NMR-spectra of 2,4-DHP-1,5-DANF-III copolymer resin

3.6 Scanning Electron Microscopy

The SEM photograph obtained at different magnification for the copolymer resin 2,4-DHP-1,5-DANF-III which is depicted in Figure-6. It gives information about surface topography and defects in structure. Scanning electron microscopy has been carried to understand the inner morphology pore structure. The morphology shows fringed model and spherulites.The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of copolymer 2, 4-DHP-1, 5 DANF-III sample. It also shows the fringes model of crystalline and amorphous structure. Thus the resin is crystalline as well as amorphous or transition between crystalline and amorphous [18-21].

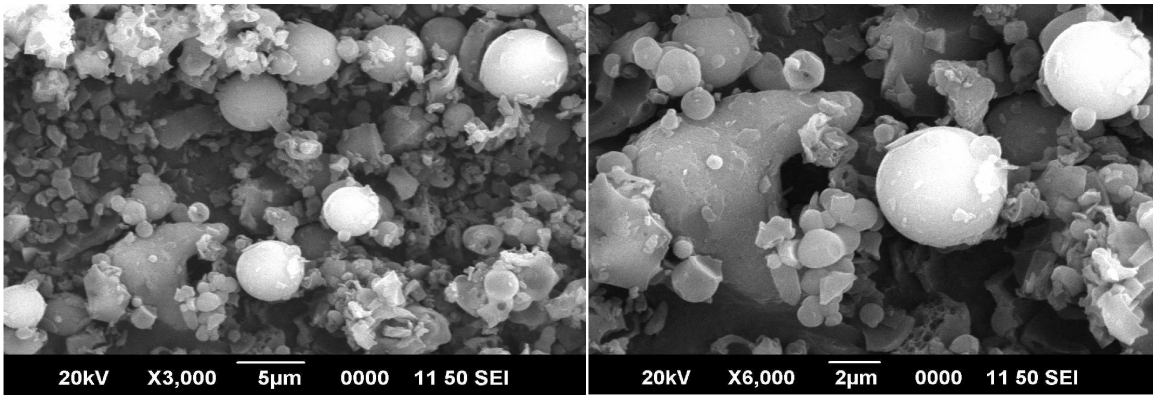

Figure 6: SEM micrograph of 2,4-DHP-1,5-DANF-III copolymer resin

IV. Conclusion

The copolymer 2,4-DHP-1,5-DANF-II was synthesized by polycondensation of 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene and formaldehyde in the presence of hydrochloric acid as catalyst. The structure of the synthesized

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copolymer was confirmed on the basis of UV-Visible, FT-IR, ^{1}H-NMR.Themolecular weight of copolymer determined by non-aqueous conductometric titration was 3238. The SEM indicates the resin is crystalline as well as amorphous or transition between crystalline and amorphous nature.

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REFERENCES

[1]. 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.

[2]. S. S. Katkamwar and W. B.Gurnule, Selective removal of toxic metal ions from waste water using phenol-formaldehyde type chelating resins, Rasayan J. Chem., 5(3), 365-375, 2012.

[3]. S. S. Rahangdale, D. D. Kamdi, J. V. Khobragade and Wasudeo B. Gurnule, Separation of toxic metals ions from waste water using pyrogallol-biuret-formaldehyde copolymer resin, I J R B A T, 8(3), 259-268, 2020.

[4]. Shavna A. Shah, Ajay V. Shah and Nayan B. Patel, A Benign approach of microwave assisted synthesis of copolymeric resin with improved thermal spectral and ion exchange properties, Iranian Polymer Journal,17(1), 3-17, 2008.

[5]. S. S. Rahangdale, S. P. Chakole, J. V. Khobragade and W. B. Gurnule,Thermal degradation studies of 2,2'dihydroxybiphenyl, ethylenediamine and formaldehyde copolymer,

[6]. Res. J. Pharm. Bio. Chem. Sci., 12(6),1-12, 2021.

[7]. Sanjay N. Niley, K. P. Kariya, B. N. Berad, Electrical conductivity study of thermally stable newly synthesized terpolymer, Technical Research Organization India, 5(1), 242-249, 2018.

[8]. M. A. Gabal, M. A. Hussein, A. A. Hermas,Synthesis, characterization and electrical conductivity of polyaniline $Mn_{0.8}Zn_{0.2}Fe_2O_4$nano-composites, Int. J. Electrochem. Sci., 11, 4526-4538,2016.

[9]. AmitN. Gupta, Electrical conductance behaviour of terpolymer resin-II derived from p-hydroxybenzaldehyde, urea and ethylene glycol, Perspectives in Science, 8, 207-209, 2016.

[10]. V. R. Chinchamalatpure and P. P. Kalbende, Synthesis, characterization and electrical conductivity of some copolymers and its polychlates, International of Scientific Research and Review, 7(3), 562-576, 2018.

[11]. W. B. Gurnule and SonaliDhote, Synthesis characterization and thermal degradation studies of copolymer derived from salicyladehyde, melamine and formaldehyde, Sci. Revs. Chem. Commun, 2(3), 403-403, 2012.

[12]. D. T. Meshram, K. P. Kariya and N. S. Bhave, Thermal degradation and electrical conductivity measurement study of resin derived from salicylic acid, hexamethylenediamine and formaldehyde, Elixir Appl. Chem., 48, 9557-956, 2012.

[13]. S.Gharbi, JameleddineKhiari and BassemJamoussi, Synthesis, characterization and chelation ion exchange studies of a copolymer resin derived from 8-hydrxyquinoline -formaldehyde-pyragallol, J. Chem. Eng. Process Technol, 5(4), 1-7, 2014.

[14]. Hayat H. A. and Roza A. Salih, Synthesis, characterization, thermal degradation and electrical conductivity of salicylidene - anthranilic acid - schiff base formaldehyde resin (R-AASA), International Journal of Advanced Research, 2(1), 1037-1040, 2014.

[15]. S. S. Rahangdale, Anil Zade and Wasudeo B. Gurnule, Cheiation ion-exchange properties of 2,4-dihydroxyacetophenone, biuret and formaldehyde terpolymer resin, E-Journal of Chemistry,6(3), 835-843, 2009.

[16]. W. B. Gurnule, Charulata S. Makde, and MudrikaAhamed, Synthesis , characterization morphology thermal, electrical and chelation ion exchange properties of a copolymer, J. Enviorn. Res. Develop. 7(3), 1183-1192, 2013.

IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 12, Issue 4, December 2021
Impact Factor: 5.731

[17]. Vaishali R. Bisen and W. B. Gurnule, Kinetics of thermal decomposition of copolymer resin derived from 4-hydroxybenzaldehyde,phenylhydrazine and formaldehyde, RJPBCS, 5(4), 1283-1297,2014.

[18]. 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).

[19]. W. B. Gurnule and Y. U. Rathod, Synthesis, Characterization and Thermal Behaviour Studies of Terpolymer Resin Derived from 8-Hydroxyquinoline-5-Sulphonic Acidand Anthranilic Acid, Current Appl. Polym. Sci., 4, 47-54 (2021).

[20]. 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)

[21]. W. B. Gurnule and N. C. Das, Kinetic Study of Non-Isothermal Decomposition of CopolymerResin Derived from 2, 4-Dihydroxypropiophenone, 1, 5-Diaminonaphthalene and Formaldehyde, Materials Today: Proceedings 15, 611–619, (2019).

[22]. Singru R. N, Zade A B, Gurnule W B et al. Thermoanalytical study and kinetics of new 8-hydroxyquinoline 5-sulphonic acid-oxamide-formaldehyde terpolymer resins. E-Journal of Chemistry 2009;6(1): S171-S182.8.