Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(10):4451-4458

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, characterization and antimicrobial activity of Resorcinol-Melamine-Formaldehyde resin

Sanjiokumar S. Rahangdale

Department of Chemistry, Jagat Arts, Commerce and Indiraben Hariharbhai Patel Science College, Goregaon-441 801, Gondia , Maharashtra, India

---

ABSTRACT

A copolymer was synthesized from resorcinol and melamine using formaldehyde as a cross linking agent at 126 ^{0}C in 2M HCl medium. The resin was characterized by elemental analysis, FTIR and NMR spectra. The RMF resin was tested for its inhibitory action against pathogenic bacteria and fungi. The resin show potent inhibitory action against bacteria such as Escherichia coli, Klebseilla, Staphylococcus aureus and Pseudomonas aeruginosa and fungi viz. Aspergillus flavus, Aspergillus niger, Pencillium species, Candida albicans, Cryptococcus neoformans and Mucor species. The copolymer resin is soluble in DMF, DMSO, THF, conc. H_2SO_4.

Keywords: Synthesis; Polycondensation; Resins; Antimicrobial screening

---

INTRODUCTION

A series of cyano derivatives of N-alkyl and N-aryl piperazine were synthesized and their antimicrobial activities were evaluated against Gram-positive and Gram-negative strain *S. Aureus, P. Aeruginosa, S. Epidermidis, E. Coli* and antifungal activities against *A. Fumigantus, A. Flavus and A. Niger*. Few of the synthesized derivatives possess potent antibacterial activity and some of the compounds were reported for its cytotoxic activity [1]. Biological evaluation of novel nitrogen containing aniline formaldehyde resin has been studied and the compounds were reported as a potent antifungal and antibacterial agent [2]. Long chain aliphatic esters as well as organic and ferrocene containing Schiff bases were synthesized and reported to have good antitumor, anticancer and antioxidant also a candidate [3]. Poly [(2-hydroxy-4-methoxybenzophenone) ethylene] resin and its polychelates with lanthanides (III) were screened for antibacterial activity and the metal chelated compounds maintain better activity compared to the ligand [4]. A copolymer involving 2, 4-dichlorophenymethacrylate and vinyl acetate was reported as a significant inhibitor for the growth of microorganisms [5]. In an earlier communication [5-9] from this department a number of such copolymers have been reported. However, no work has been carried out on the synthesis, characterization, and biological properties of the copolymer resins from resorcinol, melamine and formaldehyde.

EXPERIMENTAL SECTION

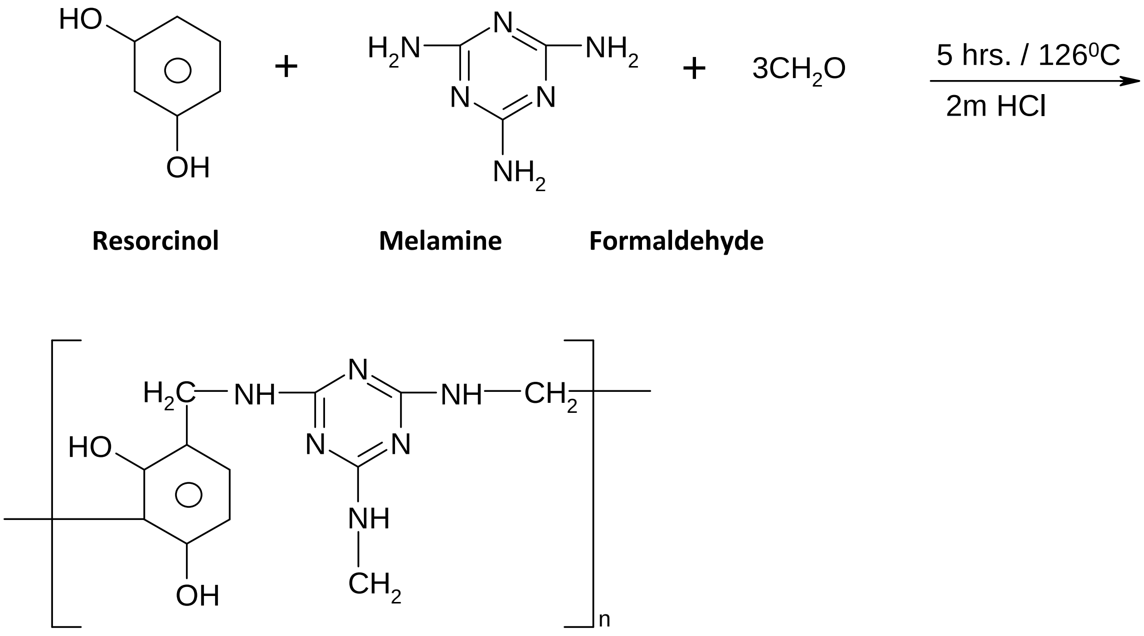
Materials

The chemicals used were all of A.R. or chemically pure grade and are procured from the market.

Synthesis of RMF copolymer resin

The RMF copolymer resin was prepared by condensing resorcinol (2.02 gm, 0.1mole) and melamine (2.522 gm, 0.1mole) with formaldehyde (21 ml, 0.3 mole) in the presence of 2M HCl (200ml) as a catalyst at 126 ^{0}C in an oil bath for 5 hrs with occasional shaking to ensure thorough mixing [10-14]. The solid resinous product obtained was removed immediately from the flask. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. Then it was extracted with diethyl ether to remove excess of p-cresol-formaldehyde copolymer which might be present along with RMF copolymer resin. The purified copolymer resin was finely ground and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 80%.

Similarly, the other copolymer resins, RMF-II, RMF-III and RMF-IV were synthesized by varying the molar proportion of the starting materials i.e., resorcinol, melamine and formaldehyde in the ratios 2:1:3, 3:1:4 and 4:1:5 respectively.



Scheme1. Reaction sequence of the synthesis of RMF resin

Characterization of the copolymers

The viscosities were determined by using Tuan-Fuoss viscometer at six different concentrations ranging from 1.00 to 0.03 % of copolymer in DMSO at 30 ^{0}C. The intrinsic viscosity $[\eta]$ was calculated by relevant plots of the Huggins' equation and Kraemmer's equation similar to earlier coworkers [15, 16, 20].

The number average molecular weights $(\overline{Mn})$ were determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. Form the graphs of specific conductance against milliequivaletns of base, first and last break were noted from which the degree of polymerization $(\overline{DP})$ and the number average molecular weight $(\overline{Mn})$ have been calculated for each copolymer resins.

Electron absorption spectra of all copolymer resins in DMSO (spectroscopic grade) were recorded on Shimadzu double beam spectrophotometer in the range of 200 to 850 nm at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh**,** Infra-red spectra of four RMF copolymer resins were recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000-400 cm^{-1} at SAIF, Punjab University, Chandigarh**,** Nuclear Magnetic Resonance (NMR) spectra of newly synthesized copolymer resins have been scanned on Bruker Avanced 400 NMR spectrometer using DMSO-d_6 at sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. SEM has been scanned by FEI-Philips XL-30 electron microscope.

Antimicrobial Screening

Biological assay depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with the known concentration of standard antibiotic. For the antimicrobial analysis the in vitro disc diffusion method has been employed. In this study the ligand and their chelates were tested for their effect on certain human pathogenic bacteria such as Gram-positive (*Aspergillus niger and Candida albicans*).

The nutrient agar medium was boiled and sterilized by autoclaving at 7 kg pressure (120 ^{0}C) for 20 min for the study of antibacterial activity. 20 mL media was poured into the sterilized petri plates and kept at room temperature for a few minutes, and allowed to solidify in plates. It was then incubated for 12 h and inoculated with microorganism using sterile swabs. All of these manipulations were carried out with utmost care under aseptic conditions. The test solution prepared by dissolving the compound in DMSO was filled with the media using a micropipette and incubated at 35 ^{0}C for 48 h. The same procedure was adopted for the antifungal studies in which potato dextrose agar was the medium.

During the course of time, the test solution diffuses and the growth of the inoculated microorganisms such as *Staphylococcus aureus, Escherichia coli, Aspergillus niger,* and *Candida albicans* were found to be affected. The activity developed on the plate was measured by measuring the diameter of the inhibited zone in millimetres. The drug ciprofloxacin was used as the standard for bacteria and nystatin for fungi.

RESULTS AND DISCUSSION

The details of reaction and elemental analysis are depicted in Table 1.

Table 1: Elemental Analysis Data, Empirical Formula of RMF Copolymer Resins

Copolymer Resin	% of Carbon observed (calculated)	% of Hydrogen observed (calculated)	% of Nitrogen observed (calculated)	Empirical formula	Empirical formula wt
RMF-I	52.60 (52.60)	4.89 (4.10)	30.00 (30.75)	$C_{12}N_6H_{13}O_2$	273
RMF-II	57.77 (57.76)	4.80 (4.90)	21.27 (21.20)	$C_{19}H_{19}N_6O_4$	395
RMF-III	60.40 (60.42)	4.80 (4.90)	16.25 (16.24)	$C_{26}H_{25}N_6O_6$	517
RMF-IV	57.26 (57.25)	4.60 (4.50)	21.65 (21.60)	$C_{37}H_{36}N_{12}O_6$	776

Viscosity measurements of all the RMF copolymer resins have been carried out at 300K in freshly triple distilled THF using Tuan-Fuoss [17] viscometer fabricated in our research laboratory. The viscometric measurements were carried out at six different concentrations ranging from 3.0% to 0.5% in a constant temperature bath with precession of ±0.1°C. The details of experimental data and calculations are furnished in Table 2 and plots for intrinsic viscosity determination are presented in Fig 1.

The intrinsic viscosity "η_{int}" has been evaluated by using modified Huggin's [17] and Kraemmer's [18] relations 'which are given below,

$$\eta_{sp} / C = \eta_{red} = \eta_{int} + K_1 [\eta_{int}]^2 \ C \qquad \text{----------Huggin's Equation}$$

$$\ln \eta_{rel} / C = \eta_{int} + K_2 [\eta_{int}]^2 \ C \qquad \text{--------------Kraemmer's Equation}$$

Where,
η_{red} = Reduced Viscosity
η_{sp} = Specific Viscosity
η_{red} = Reduced Viscosity
η_{rel} = Relative Viscosity
C = Concentration in percent (w/v)
K_1 = Huggin's constant
K_2 = Kraemmer's constant

The reduced viscosity η_{red} of the copolymer resin samples was calculated by the formula η_{sp}/C, from the Huggin and Kraemmer relations given above it is clear that the plots η_{sp}/C i.e. ηred and η_{rel}/C versus C would be linear. The value of intrinsic viscosity "η_{int}" has been calculated from the intercepts on the basis of viscosity function of both the plots. The values of intrinsic viscosity obtained from both the plots are found to be identical. It is observed that, the value of intrinsic viscosity increases with the increase in molecular weight of copolymer resins (Table 2). It is in good agreement with the trend observed and explained by earlier research workers.

Table 2: Viscometric Data for RMF – I Copolymer Resin

Solvent : Tetrahydro Furan (THF)
Temperature : 313 ±0.1 K
Efflux time of pure solvent (t_o) =149.2 sec

Polymer concentration 'C' (gdl-1)	Efflux time for solution 't'	Relative viscosity $\eta_{rel} = \frac{t}{t_o}$	Specific viscosity $\eta_{sp} = \left(\frac{t - t_o}{t_o}\right)$	Reduced viscosity ηred = ηsp/C (dlg-1)	In ηrel	In ηrel/C
0.5	152.8	1.0241	0.0241	0.0482	0.0238	0.0476
1.0	156	1.0455	0.04557	0.04557	0.0445	0.0445
1.5	158.4	1.0616	0.0616	0.04110	0.0598	0.0398
2.0	160.2	1.0737	0.0373	0.0368	0.0711	0.0355
2.5	161.4	1.0817	0.0817	0.03270	0.0785	0.0319
3.0	162.2	1.0871	0.0871	0.02904	0.0835	0.0278

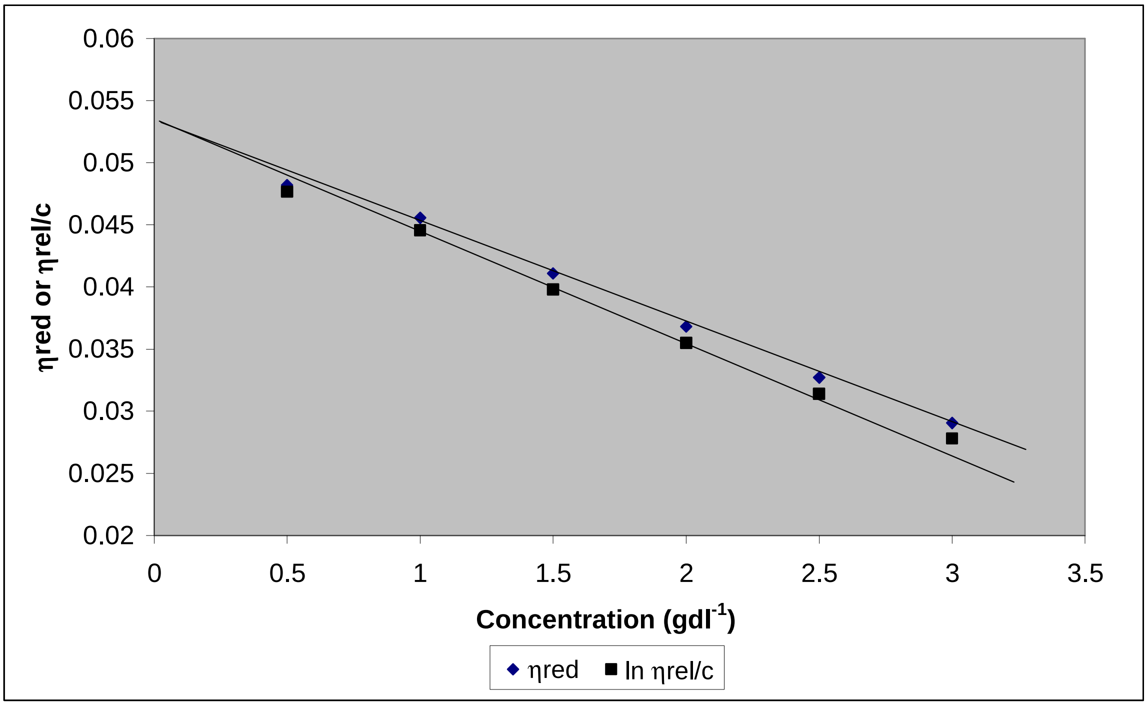


Fig.1: Viscometric Plots of RMF –I Copolymer Resins

The electronic spectra of all RMF resins are shown in Fig 2. All the copolymers gave rise to two characteristic bands at 240-260 nm and 320 nm. These observed positions of the absorption bands indicate the presence C=N- group. The appearance of former band (more Intense) can be accounted for π□→ π* transition while the latter band (less intense) may be due to n → π* electronic transition.

The shift towards longer wavelength i.e. bathochromic shift from the basic value (viz.260 and 320 nm respectively) may be due to conjugation effect and presence of phenolic hydroxy group (auxochrome) is responsible for hyperchomic effect i.e. higher ε_{max} values [19, 21].

From the spectra of RMF copolymer resins it is observed that ε_{max} value gradually increases in the order given below

RMF- I < RMF- II < RMF- III < RMF- IV.

The above increasing order of ε_{max} values may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic- OH group) in the repeated unit (monomer) of the copolymer resins [20, 25]. This observation is in good agreement with proposed structures of above copolymer resins and it is further supported by other spectrometric studies such as infra-red and proton nuclear magnetic resonance spectra.

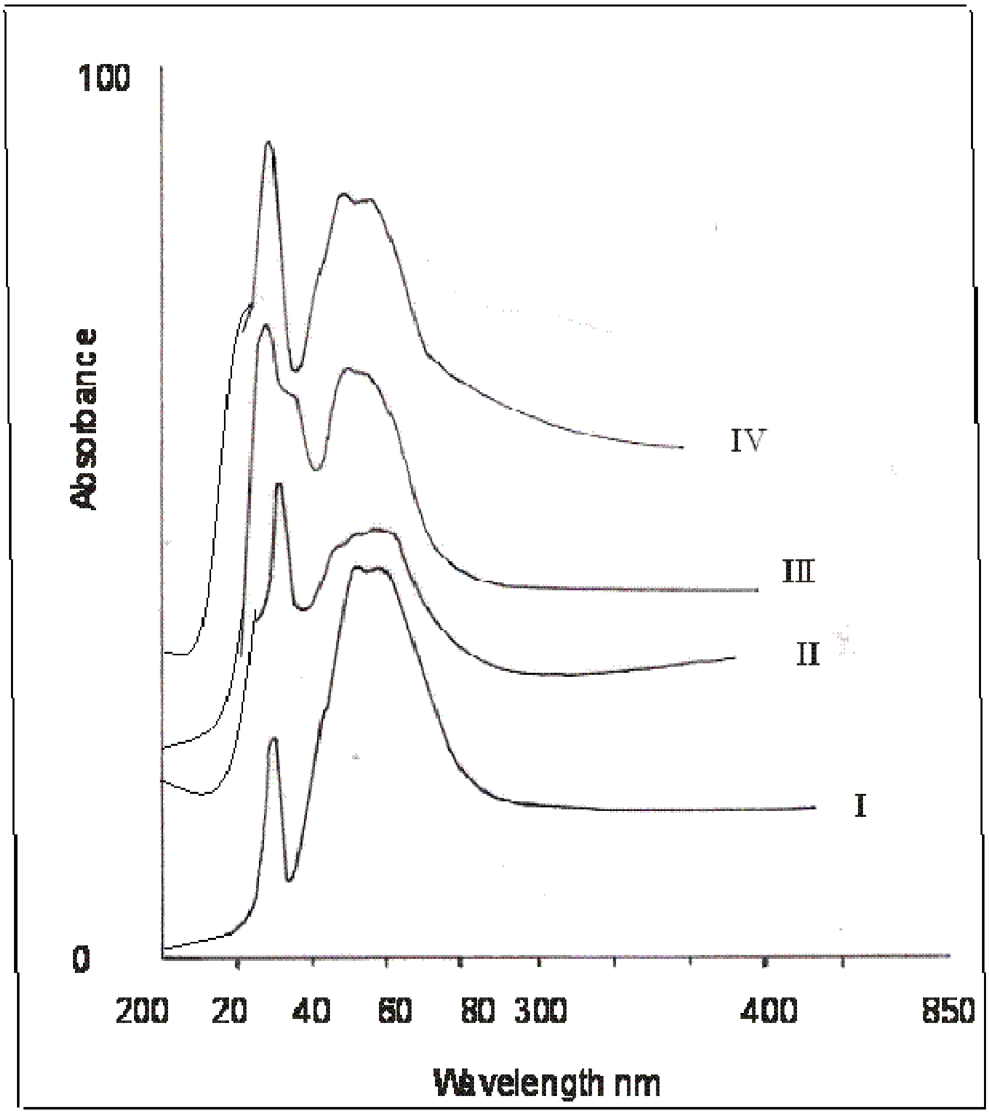


Fig. 2: UV-visible spectra of RMF Copolymer Resins

The IR spectra of RMF copolymer resins are presented in Fig. 3.

The IR spectral studies of RMF resin that all these copolymers give rise to nearly similar pattern of spectra. The assignment of vibrational frequencies is mainly based on the data available in the literature. A broad band appeared in the region 3344-3348 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding. The presence of -NH in melamine moiety may be assigned due to sharp band at 3212 -3214 cm^{-1} [21]. A sharp peak at 1530-1532cm^{-1} may be ascribed to aromatic skeletal ring [20]. A sharp peak at 1615- 1617 cm^{-1} may be due to the stretching vibration of melamine group. The bands obtained at 785cm^{-1} suggests the presence of methylene bridges [20, 23] in the polymer chain.

NMR spectra of all RMF copolymer resins are taken in DMSO-d6 solvent. The spectra are presented in Fig. 4.

The NMR spectra of RMF copolymer resins show a weak multiplate signal (unsymmetrical pattern) in the region 6.4 – 6.7 (δ) ppm which is due to aromatic protons. A medium singlet peak appeared at 2.3 – 2.5 (δ) ppm may be assigned to methyl protons of Ar-CH2-NH group. All the Four polymers viz. RMF-I ,RMF-II RMF -III and RMF-IV copolymer resins exhibit signals in the region 3.3 which may be due to methylene Bridge.

The microbial screening results of RMF copolymer ligand show (Table 3) higher activity is due to the donor atoms of the ligand and the π-electrons delocalization. This effect increases the lipophilic character, which favours the permeation through the lipoid layer of the bacterial and fungal membranes. The higher activity may also be due to the presence of - OH and the aromatic ring [27]. It is perceived that the factors such as solubility, conductivity, dipole moment and cell permeability mechanism may be alternative reasons for the increased activity of the metal complexes [28]. The ligand has good inhibition against the growth of Gram-negative bacteria which induces tumour. Hence the copolymer ligand may possess antitumor activity. The Gram-positive bacteria are both pathogenic and invasive. The copolymer has good inhibition characteristics against the growth of this pathogen. *Aspergillus niger* cause aspergillosis, the growth of the fungus is controlled by the copolymer chelates to some extent. The *Candida albicans* can penetrate into the intestinal walls and cause diseases. From the findings, the growth of *Candida albicans* is inhibited by the addition of RMF copolymer resin.

Table 3. Antimicrobial activities of RMF copolymer resin.

Copolymer	Diameter of zone of inhibition (mm)			
	S. Aureus	*E. Coli*	*A. Niger*	*C. Albicans*
RMF	10	11	12	10
Solvent (DMSO)	--	--	--	--

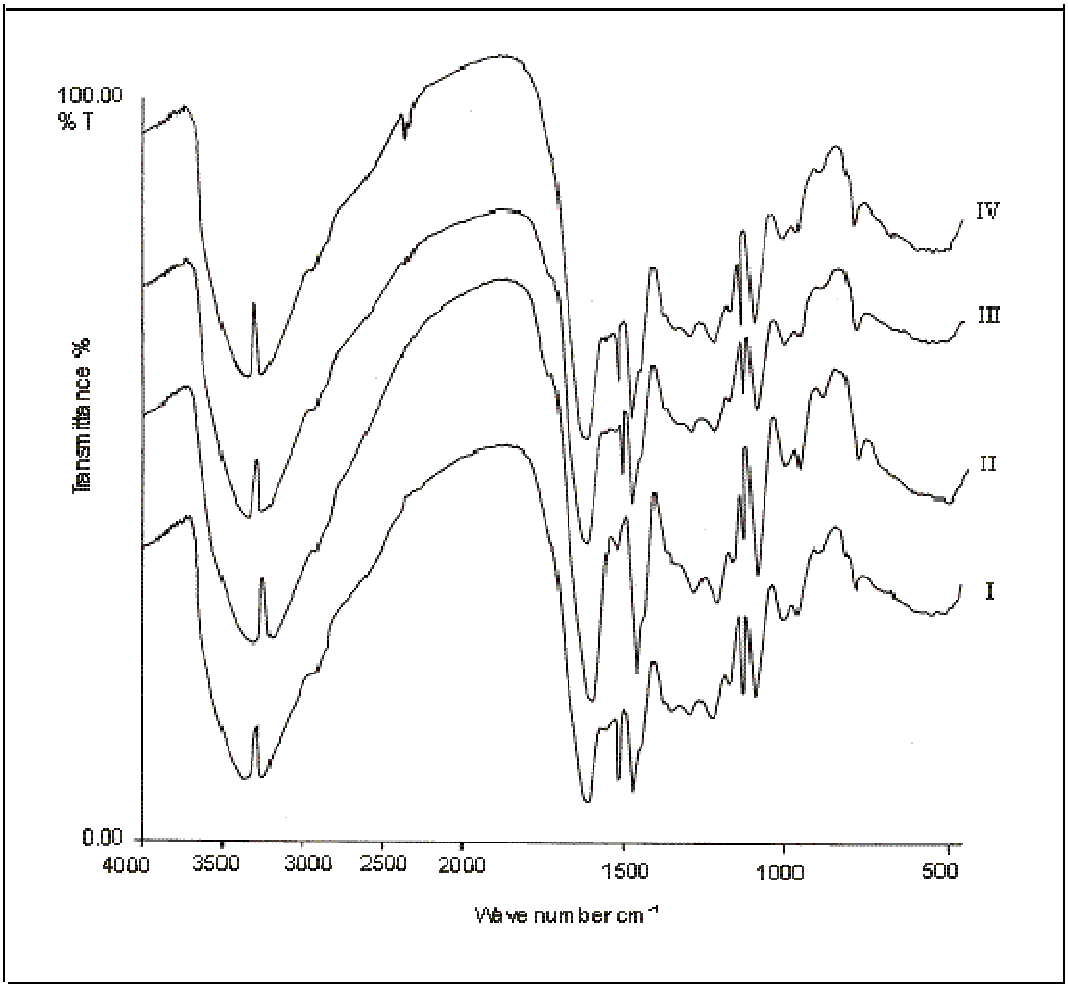


Fig. 3: Infrared Spectra of RMF Copolymer Resins

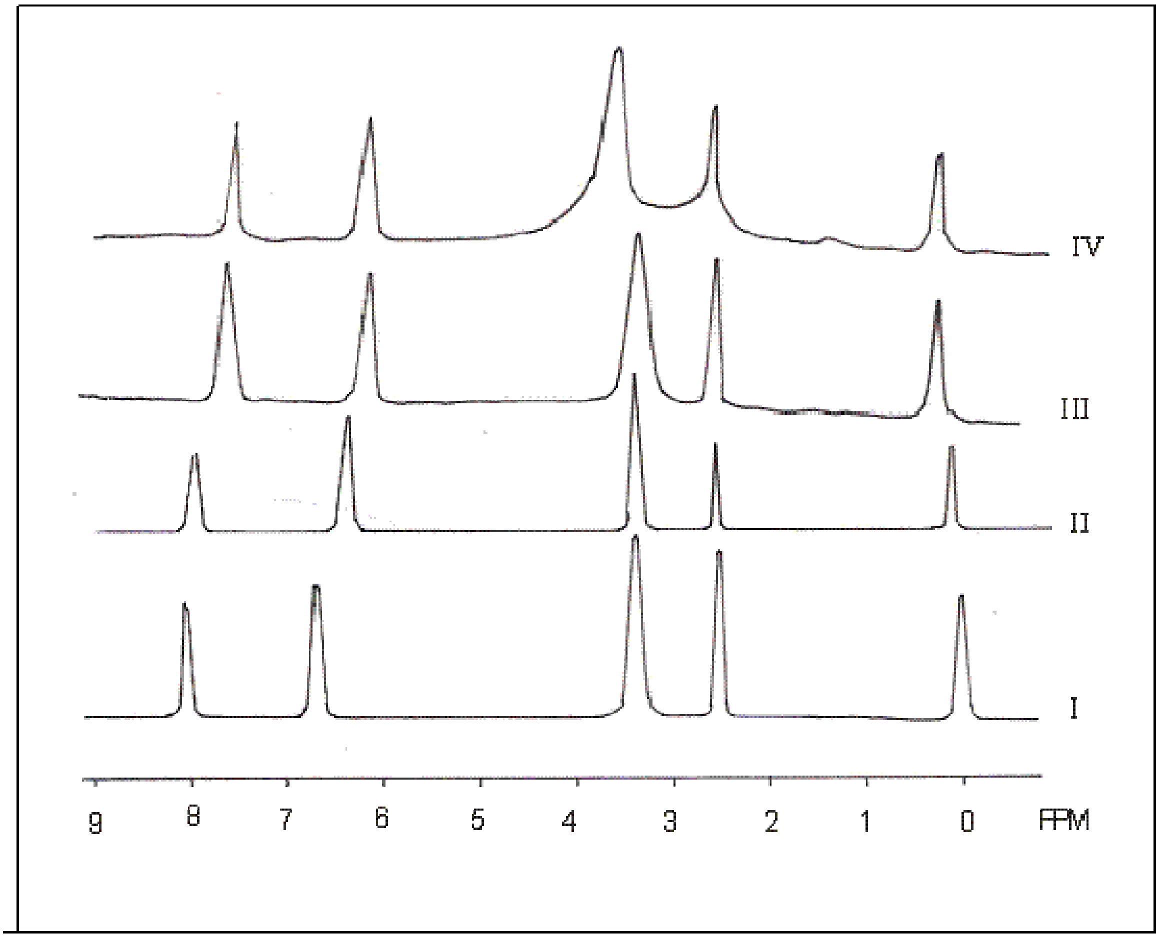


Fig: 4: Nuclear Magnetic Resonance Spectra of RMF Copolymer Resin

Acknowledgements

The author expresses their sincere thanks to The Director, Laxminarayan Institute of Technology, Nagpur, India for providing necessary laboratory facilities and UGC for financial support.

CONCLUSION

A copolymer RMF based on the condensation reaction of resorcinol and melamine with formaldehyde in the presence of acid catalyst was prepared. The copolymer resin shows higher activity against certain bacterial strains such as *Staphylococcus aureus, Escherichia coli,* and fungal strains *Aspergillus niger* and *Candida albicans.*

REFERENCES

[1] P Chaudhary, S Nimesh, V Yadav, AK Verma, R Kumar, *Europ. J. Med. Chem.*, **2007**, 42, 471.
[2] S Parveen, T Ahamed, A Malik, N Nishant, *Polym Adv Tech.*, **2008**, 19, 1779.
[3] H Nawaz, Z Akhtar, S Yameen, HM Siddiqi, B Mirza, A Rifat, *J Org Chem.*, **2009**, 604, 2198.
[4] MM Patel, MA Kapadia, GP Patel, JD Joshi, *React Funct Polym.*, **2007**, 67, 746.
[5] RN Singru, *J. Chem. Pharm.Res.*, **2012,** 4(1), 46-53.
[6] RN Singru, WB Gurnule, *Iran Polym J.*, **2010**, 19 (3), 1-15.
[7] WB Gurnule, HD Juneja, LJ Paliwal, *React Funct Polym.*, **2002**, 50, 95-100.
[8] WB Gurnule, DB Patle, *Polym Bull.*, **2011**, 66, 803-820.
[9] VD Mane, NJ Wahane, WB Gurnule, *J Appl Polym Sci.*, **2009**, 111, 3039-3049.
[10] M Jadhao, LJ Paliwal, NS Bhave, *J. Appl. Polym. Sci.*, **2005,** 96, 1605.
[11] AN Gupta, VV Hiwase, AB Kalambe, *J Chem Pharma Res*, **2012,** 4(5), 2475-2482.
[12] SS Rahangdale, WB Gurnule, *Der Pharma Chemica*, **2011,** 3(4), 314-322.
[13] DN Urade, VV Hiwase, AB Kalambe, *J Chem Pharma Res*, **2012,** 4(1), 732-740.
[14] SS Rahangdale, AB Zade, WB Gurnule, *E-journal of Chemistry*, **2009,** 6, 835.
[15] MV Tarase , AB Zade, WB Gurnule, *J. Appl. Polym. Sci.*, **2008,** 108, 738.

[16] H Dudley, I Fleming, Spectroscopic methods in Organic Chemistry; McGraw-Hill: UK, 1975.
[17] RM Silverstein, GC Bassler, *Spectrometric Identification of Organic Compounds*, 2nd Ed; Wiley: New york, **1967**, 80.
[18] RN Singru, WB Gurnule, *Iran. Polym. J.*, **2010**, 19(3), 1.
[19] PK Roy, AS Rawat, V Choudhary, PK Rai, *J. Appl. Polym. Sci.*, **2004**, 94, 1771.
[20] K Nakanishi, *Infrared Absorption Spectroscopy Practical*; Noldden Day, INC and Nankodo Co Ltd: Tokyo, **1964**, 20.
[21] IJ Ballemy, *The IR Spectra of Complex Molecules*; John Wiley Sons. Inc., New York, **1958**, 42.
[22] PEP Michel, JM Barbe, HD Juneja, LJ Paliwal, *Eur. Polym. J.*, **2007,** 42, 4995.
[23] RN Singru, WB Gurnule, *J. Therm. Anal. Calorim.*, **2010,** 100, 1027.
[24] SA. Patel, BS Shah, RM Patel, PM Patel, *Iran. Polym. J.*, **2004,** 13, 445.
[25] FA Cotton, G Wilkinson , *Advanced Inorganic Chemistry*, 3rd ed., Wiley, New York, **1972**, 52.
[26] BA Shah, AV Shah, RR Bhatt, *Iran. Polym. J.*, **2007,** 16(3), 173.
[27] N Singh, S Gupta, G Nath, *Central National De La Recherche Scientifique* (CAT. INIST) **2000**, 14, 484.
[28] GB Bagihalli, SA Patil, PS Badami, *J Iran Chem Soc*., **2009**, 6 (2), 259.