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Research Article

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Structural and Antibacterial study of Resin-II Derived from p-Nitrophenol, Resorcinol and Formaldehyde

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ABSTRACT

The resin(abbreviated as PNPRF-II) was derived from acid catalyzed polycondensation of p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) using 1M HCl at 120-125^{0}C. The tentative structure of this resin was determined by elemental analysis, ^{1}H NMR, FT-IR and UV-Vis spectra. The molecular weight was determined by non-aqueous conductometric titration. The antibacterial activity relative to ampicilin for this resin was determined against gram +ve and gram –ve bacteria.

Key Words: Terpolymer, Polycondensation, Resin, Antibacterial activity, spectral study.

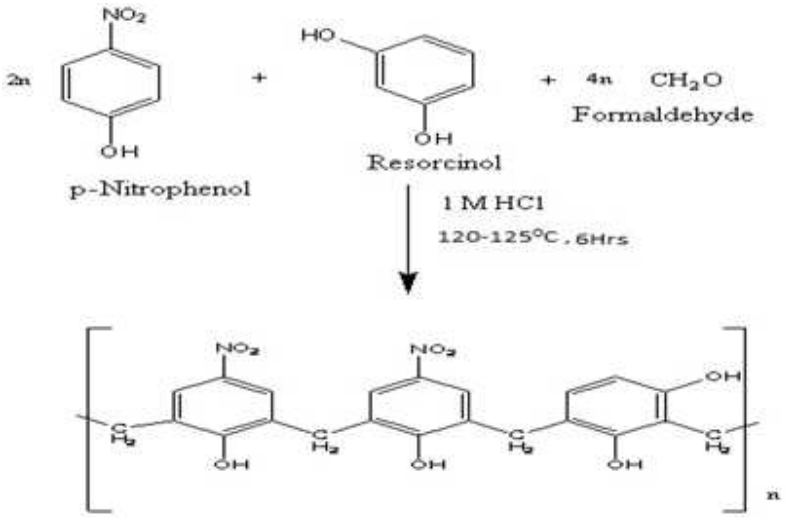
INTRODUCTION

The application of polymers in all spheres of life has been abundantly increased in recent years. Although various workers have synthesized many polymers but there is a noteworthy demand to synthesize eco-friendly polymers having some biological activities like antifungal and antibacterial. The invasion of polymers by fungi, bacteria and other organism is manifested by loss of mechanical properties, surface degradation, discoloration, staining and other deteriorations [1, 2]. Resorcinol-acetophenone copolymer was prepared [3] by using trifluoroacetic acid as catalyst having some antimicrobial activity. Similarly, 2, 4-dihydroxybenzaldehyde oxime-formaldehyde polymers were synthesized [4] in the presence of oxalic acid as a catalyst. The oxime carbazone and thiosemicarbazone derivative of N (4-acetylphenyl) maleimide was radical homopolymerized and they show good antimicrobial activities [5]. Literature survey reveals that antimicrobial activity of copolymer resin derived from 2, 2'-dihydroxybiphenyl, dithiooxamide and formaldehyde was studied [6]. Synthesis, characterizations, with antimicrobial activity of acrylic copolymers derived from 2, 4-dichlorophenyl acrylate was studied by Patel *and* coworkers [7].Various researchers have been studied the application of terpolymer resins of substituted phenols and formaldehyde [8]. Synthesis and characterization with good antimicrobial activity of important heterocyclic acrylic copolymers were studied [9]. Terpolymers of salicylic acid, thiourea with trioxane and 2-hydroxy -4 methoxyacetophenone, thiourea with trioxane and p-hydroxybenzoic acid, melamine with formaldehyde have been reported in literatures [10-13].Recently Hiwase *et al* have characterized p-hydroxybenzaldehyde-resorcinol-formaldehyde and p-hydroxyacetophenone-hexamine-formaldehyde [14-15]. Dharkar *et al* charectarised the acid catalyzed terpolymer resin of melamine-aniline-formaldehyde with various informative applications [16]. The present paper deals with the structural characterization of p-nitrophenol-resorcinol-formaldehyde (PNPRF-II) terpolymeric resin by various physicochemical studies and relative antibacterial activity against gram +ve and gram –ve bacteria.

EXPERIMENTAL SECTION

All chemicals were AR grade or chemically pure grade. p-Nitrophenol, resorcinol and formaldehyde were procured from Sd fine, India. Triple distilled water was used for all the experiments.

Synthesis of p-nitrophenol-resorcinol-formaldehyde terpolymer resin (PNPRF-II):
A mixture of p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) was refluxed in presence of 1M HCl (150ml) in oil bath at 120-125^{0}C for six hours with intermittent shaking. The resinous reddish-brown colored product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The powder product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with diethyl ether to remove p-nitrophenol-formaldehyde co-polymer and resorcinol-formaldehyde copolymer. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipited by gradual drop wise addition of 1:1 HCl with constant and rapid stirring to avoid the lump formation. The **PNPRF-II** resin so obtained was filtered, washed several times with hot distilled water. The yield of **PNPRF-II** terpolymer resin was found to be 73.05%.



PNPRF-II

Scheme: Synthesis of PNPRF-II Resin

Table 1: Synthetic details PNPRF-II resin

Resin	p-nitrophenol	Resorcinol	Formaldehyde	Catalyst 1M HCl	React. Temp (^{0}C)	Time (hrs)	Yield %
PNPRF-II	0.2M	0.1M	0.4M	150ml	120-125	6	73.05

RESULTS AND DISCUSSION

Characterization of PNPRF-II resin
PNPRF-II resin was buff, reddish –brown colored. The synthesized PNPRF-II resin was mostly soluble in DMF, DMSO and aq. NaOH. The resin was insoluble in acids and common organic solvents.

Elemental analysis and molecular weight determination

Elemental analysis were carried out at CIMFR unit, Nagpur, by analytical Functional Testing Vario MICRO CHN elemental analyzer (Germany), Serial no-11083059.The number average molecular weight(M_n)was determined by non-aqueous conductometric titration in DMF using 0.1M KOH in absolute alcohol as titrant.From the graphs of specific conductance against miliequivalents of base, first and last break were noted .The degree of polymerization (DP) and the number average molecular weight (Mn) have been calculated for terpolymer resin PNPRF-II using following equations,

DP= (Total mili equivalents of the base required for last break)/(miliequivalents of base required for first break.)

Mn = DP x Molecular weight of the repeating unit

The repeating Unit weight was obtained from elemental analysis.

The elemental analysis and molecular weight determination data of **PNPRF-II** resin are given in following Table-2.

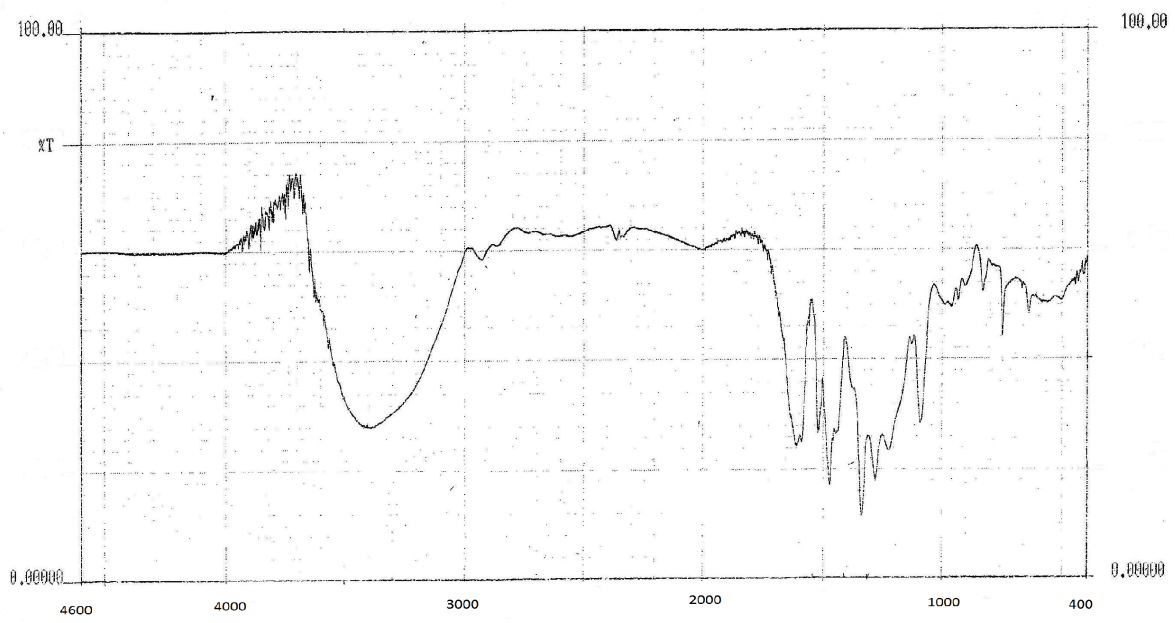
Table 2: Elemental analysis and molecular weight determination of PNPRF-II Resin

Resin	%C		%H		%N		*DP (n)	Molecular weight (M_n)	Mol. Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found				
PNPRF-II	60.27	60.01	4.1	4.07	6.39	6.53	31	9198	$C_{22}H_{18}N_2O_2$	438

Spectral analysis

IR spectrum of PNPRF-II resin

IR spectra of synthesized terpolymeric resin were recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu, model No-8101A. FT-IR spectrum of PNPRF-II resin is shown in Fig.1. and FT-IR spectral data is given in following Table-3.



Wavenumber (cm^{-1})

Fig. 1. FT- IR spectrum of PNPRF – II resin

Table 3: FT-IR data of PNPRF-II resin

PNPRF-II Freq. cm^{-1}	Assignment
3353	H- Bonded Phenolic -OH
2939	CH- Str.
1560, 1338	Ar-NO_2
992.8	*Pnp-CH_2-Pnp, CH- def.
933.7	Res-CH_2-Pnp, CH-def
831	1,2,3,4 tetra substituted aromatic ring
1223, 1088	1,2,3,5 tetra substituted aromatic ring

*Res-Resorcinol,*Pnp–p-Nitrophenol moiety*

The broad band at 3353 cm^{-1} was assigned to stretching vibration of hydrogen bonded phenolic group [17]. The absorption at 2939 cm^{-1} was assigned to-CH_2- stretch shows the bridges of CH_2 in PNPRF-II resin[18].The peaks at 1338 cm^{-1} and 1560 cm^{-1} was attributed to (N=O) for symmetrical and asymmetrical stretch respectively . The weak band at 992.8 cm^{-1} represents the C-H deformation in pnp-CH_2-pnp moiety. The weak band at 933.7 cm^{-1} was assigned to the C-H deformation in res-CH_2-pnp moiety. Moreover the absorption at 831 cm^{-1} was attributed to 1, 2, 3, 4 tetra substituted aromatic ring and the bands at 1223 cm^{-1}, 1088 cm^{-1} were attributed to 1, 2, 3, 5 tetra substituted aromatic ring respectively[19] .

^{1}H NMR Spectrum of PNPRF-II resin

^{1}H NMR spectra of terpolymeric resin using DMSO-d^6 solvent were scanned on BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh. The ^{1}H NMR spectral data is tabulated in Table- 4. The ^{1}H NMR spectrum of PNPRF-II resin is shown in Fig.2. The NMR characterization of resin is based on data available in literature [20].The signal at 5.1δ ppm was attributed to Phenolic –O**H** (pnp-moiety). The signals at 7.6 δppm was due to aromatic proton in PNPRF-II terpolymeric resin. Signal at 2.5 δppm was assigned to –H protons in pnp-C**H_2**-Res moiety .Signal at 2.07 δppm was due to C-H protons in pnp-C**H_2**-pnp moiety in PNPRF-II resin.

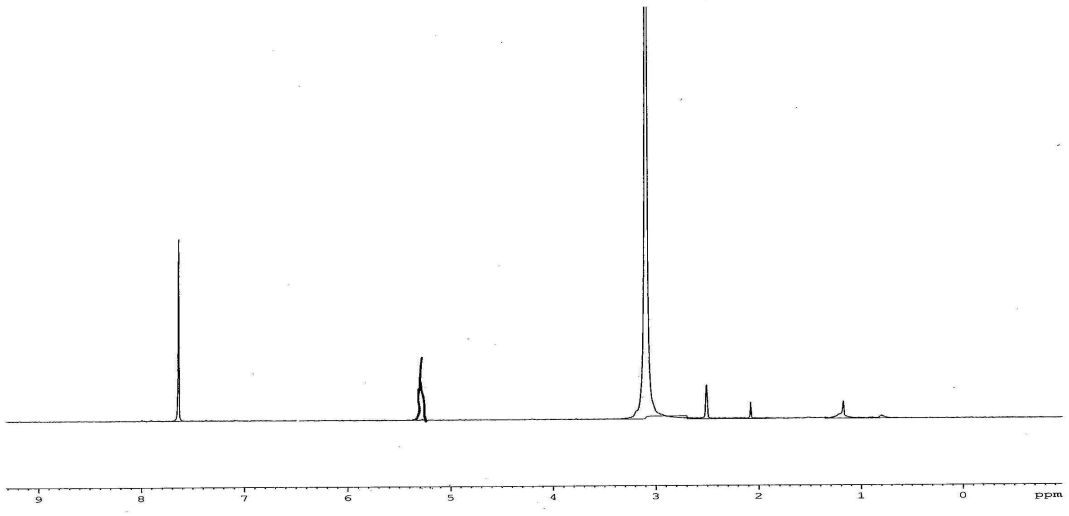


Fig.2. ^{1}H NMR spectrum of PNPRF – II resin

Table 4:^{1}H-NMR data of PNPRF-II resin

PNPRF-II δppm	Nature of proton assigned
2.5	Pnp-C**H**$_2$-Res
2.07	Pnp-C**H**$_2$-Pnp
7.6	Aromatic- **H**
5.1	Phenolic - O**H**(Pnp moiety)

UV-Vis spectrum of PNPRF-II resin

UV-Vis spectra of terpolymer resin in DMSO Solvent recorded by UV-Vis Double Beam Spectrophotometer Schimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy, RTM Nagpur University, Nagpur. The UV-Vis spectrum of PNPRF-II resin is shown in Fig-3. The UV-Vis spectral data is given in Table-5.

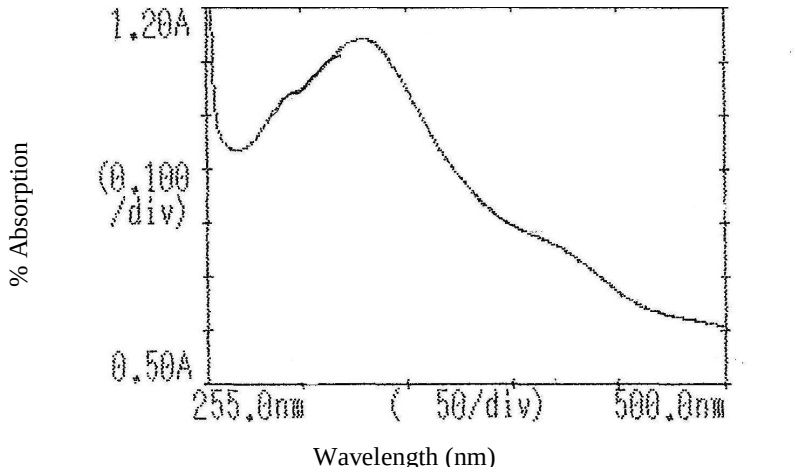


Fig. 3. UV-Vis spectrum of PNPRF-II resin

Table 5: UV-Vis data of PNPRF-II resin

Resin	Wavelength,nm range for n-π* transition	Wavelength,nm range for π–π* transition	Group(moiety)
PNPRF-II	433	328	Pnp -NO_2

Spectra depicted two characteristic bands in the resin of 328 nm and 433 nm in PNPRF-II resin [21-22].The band at 328 nm indicates the presence of -NO_2 group containing N=O bond in conjugation with an aromatic nucleus and was assigned to of π–π* transition while the hump in the region of 433 nm was due to n-π* electronic transition.

Antibacterial activity of PNPRF-II resin

Antibacterial activity of resin was studied against gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and gram negative bacteria (*Escherichia coli*) at suitable concentration by Mueller Hinton Agar method [23-25]. DMSO solvent was used as control in this method. The inhibition zone was measured as diameter in four directions and expressed as mean. The result was compared using ampicilin (200μg/ml), a broad spectrum antibiotic as reference. % Zone of inhibition for resin sample is shown in Table-6.

Table 6: Antibacterial data of PNPRF-II resin

% Zone of inhibition									
Resin	**Gram+ve**						**Gram -ve**		
	B.subtilis			***S. aureus***			***E. coli***		
Concentration (µg/ml)	200	400	600	200	400	600	200	400	600
PNPRF-II	4.54	33.55	66.44	3.57	14.78	27.18	22.64	47.71	81.63

CONCLUSION

The data of Elemental analysis, UV–Vis spectra, FT-IR spectra, ^{1}H NMR spectra, non aqueous conductometric titration supports to the above tentative structure of PNPRF-II terpolymeric resin. Antibacterial activity results shows significant % zone of inhibition against gram +ve and gram –ve bacteria. It is more toxic to gram –ve than gram +ve. The data suggest that toxicity increases with increase in concentration of resin.PNPRF-II resin is less toxic to S.*aureus* as compared to B.*substilis* among gram +ve.

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