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Semiconducting behavior and antibacterial activity of some resins derived from p-Nitrophenol, Resorcinol and Formaldehyde

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ABSTRACT

The resins PNPRF-I and PNPRF-II were derived from acid catalyzed polycondensation using 1M HCl at 120-125^oC by varying monomer composition ratio. The resin obtained by condensing p-nitrophenol (0.1M), resorcinol (0.2M) and formaldehyde (0.4M) was abbreviated as PNPRF-I. Similarly the resin prepared by monomer composition p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) was abbreviated as PNPRF-II. The tentative structures of these resins were determined by elemental analysis, ¹H NMR, FT-IR and UV-Vis spectra. The molecular weight determinations were carried out by non-aqueous conductometric titrations. The conductivities of PNPRF-I and PNPRF-II were found to be in range 0.096 x 10⁻⁶ to 0.3294 x 10⁻⁶ and 0.0681x 10⁻⁶ to 3.1316 x 10⁻⁶ mho cm⁻¹ respectively for temperature range 343-573K. The activation energies of conduction for PNPRF-I and PNPRF-II were found to be 4.089 kJ mol⁻¹ and 5.365 kJ mol⁻¹. The antibacterial activities relative to ampicilin for these resins were determined against gram +ve and gram -ve bacteria.

Keywords: Terpolymer, Polycondensation, Resin, Antibacterial activity, Electrical conductivity.

INTRODUCTION

The semi conducting property of terpolymer resins have gained sufficient ground in recent years. Electrically conducting polymer resin is undoubtedly one of the focal points of current interest in solid state physics and chemistry. Their discovery has led to the emergency of not only new type of material capable of replacing expensive metals but also new concept to explain their high conductivity. Work on organic conducting polymers has been carried out extensively due to wide applicability in area of electronics [1]. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, protective adhesives and aerospace industries because of their chemical resistance and electrical insulation properties [2]. Various

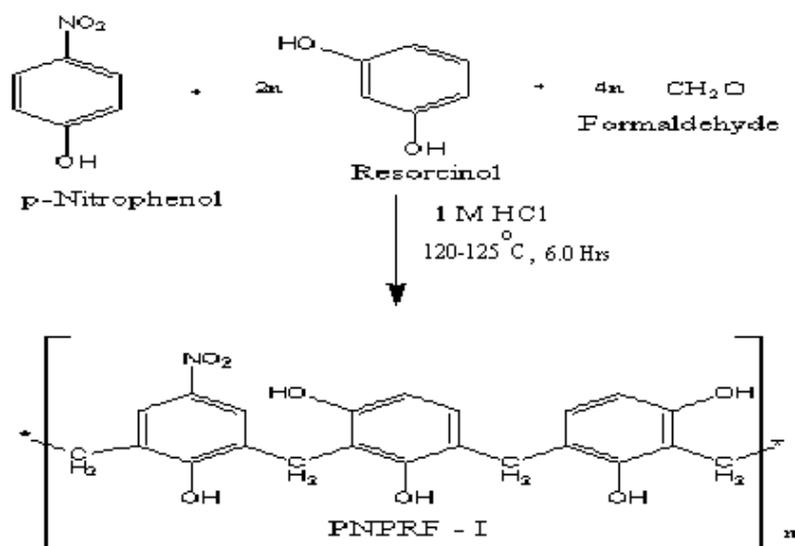
researchers were synthesized and characterized the formaldehyde based terpolymeric resins using various functional phenols as one of the monomer [3-7]. Synthesis and characterization with good antimicrobial activity of important heterocyclic acrylic copolymer were studied [8]. Recently Hiwase *et al* have characterized p-hydroxybenzaldehyde-resorcinol-formaldehyde and p-hydroxyacetophenone-hexamine-formaldehyde [9-10]. Dharkar *et al* studied the conductivities of melamine-aniline-formaldehyde terpolymer resins and its polychelates. The activation energy values were found to be in range of 0.847 to 1.156 eV [11]. Conducting property of resin was reported due to delocalized p electrons of aromatic systems in polymer matrix.

The present paper deals with the characterization, conducting nature and antibacterial activity of p-nitrophenol-resorcinol-formaldehyde (PNPRF) terpolymeric resins.

MATERIALS AND METHODS

2.1. Chemicals

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



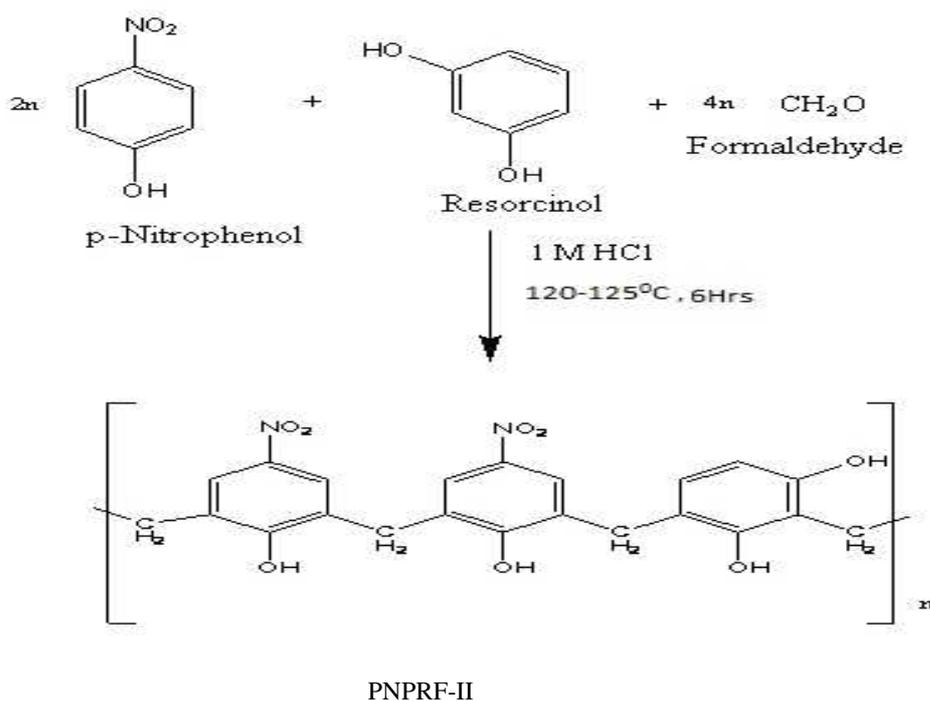
Scheme 1: Synthesis of PNPRF-I Resin.

2.2. Synthesis of p-nitrophenol-resorcinol-formaldehyde terpolymer resins

A mixture of p-nitrophenol (0.1M), resorcinol (0.2M) and formaldehyde (0.4M) was refluxed in presence of 1M HCl (150ml) in oil bath at 120-125^oC for six hours with intermittent shaking. The resinous redish-brown colored product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove p-nitrophenol-formaldehyde and resorcinol –formaldehyde copolymer which might be produced

along with terpolymer. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The **PNPRF-I** resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer **PNPRF-I** was found to be 73.34%

Similar procedure was carried out for the preparation and purification of **PNPRF-II** terpolymeric resin by condensing p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M). The yield **PNPRF-II** was found to be 73.05%.



Scheme 2: Synthesis of PNPRF-II Resin

Table 1. Synthetic detail of PNPRF resins

Resin	p-nitrophenol	Resorcinol	Formaldehyde	Catalyst 1M HCl	React. Temp (^o C)	Time (hrs)	Yield %
PNPRF-I	0.1M	0.2M	0.4M	150ml	120-125	6	73.34
PNPRF-II	0.2M	0.1M	0.4M	150ml	120-125	6	73.05

RESULTS AND DISCUSSION

2.3. Characterization of PNPRF resins

2.3.1. Elemental analysis and molecular weight determination of PNPRF resins

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 weights (M_n) were determined by non-aqueous conductometric titration in DMF using 0.1M KOH in absolute alcohol as titrant. From the graphs of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (M_n) was calculated for each terpolymer resin using following equations,

$$DP = (\text{Total milliequivalents of the base required for last break}) / (\text{milliequivalents of base required for first break.})$$

$$M_n = DP \times \text{Molecular weight of the repeating unit}$$

The repeating Unit weight was obtained from elemental analysis.

The Elemental analysis and molecular weight determination data of PNPRF resins are given in following Table 2.

Table 2. Elemental analysis and molecular weight determination of PNPRF resins

Resin	%C		%H		%N		*DP and Molecular weight (M_n)		Mol. Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found				
PNPRF-I	64.54	64.31	4.64	4.72	3.42	3.91	30	12270	$C_{22}H_{19}NO_7$	409
PNPRF-II	60.27	60.01	4.10	4.07	6.39	6.53	31	9198	$C_{22}H_{18}N_2O_2$	438

2.3.2 IR spectra of PNPRF resins

IR spectra of synthesized terpolymeric resins were recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu, model No-8101A. FT-IR spectra of PNPRF resins are shown in Figure1. and Figure2 FT-IR spectral data are given in following Table 3.

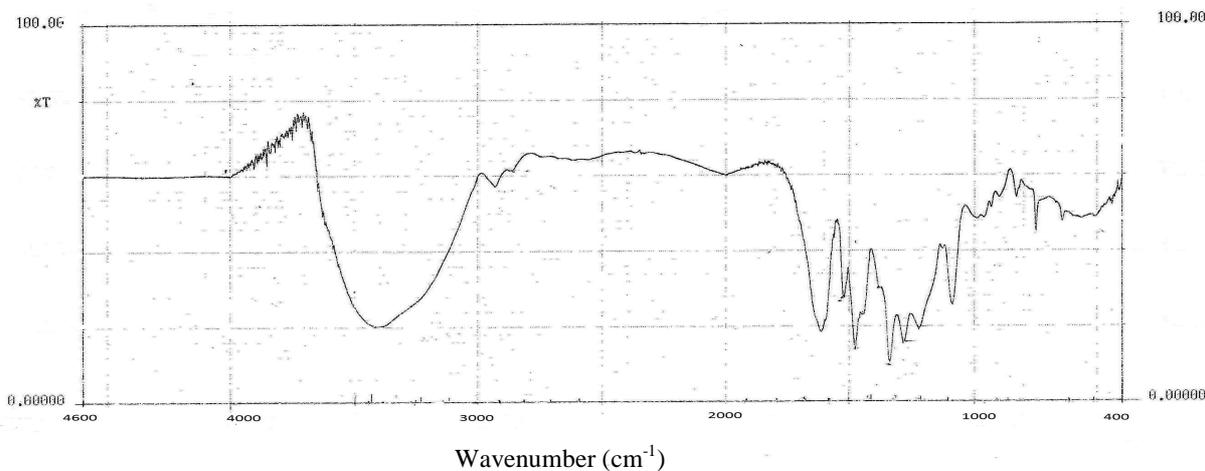


Figure 1: FT IR spectra of PNPRF – I resin

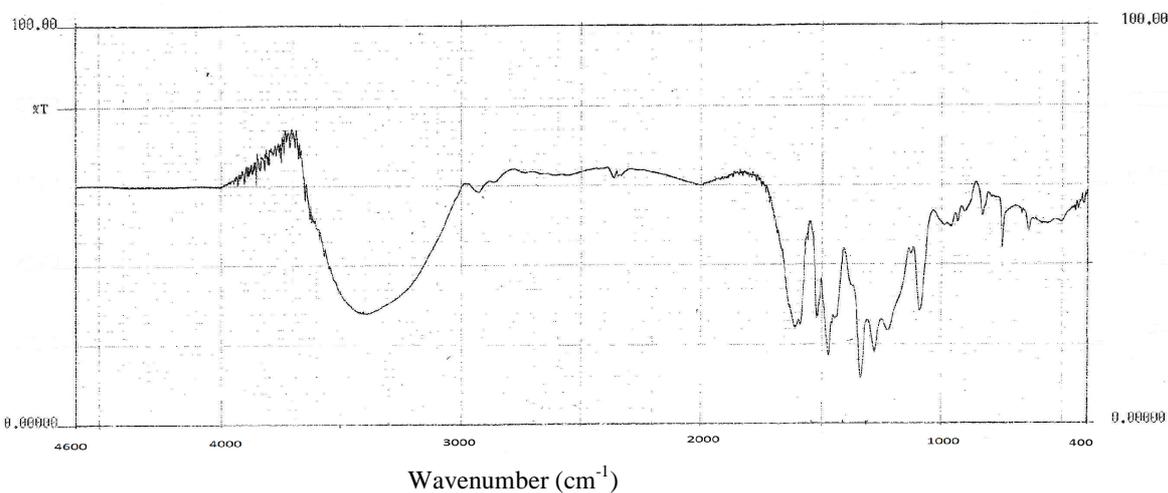


Figure 2: FT IR spectra of PNPRF – II resin

Table 3. FT-IR data of PNPRF resins

PNPRF-I Freq.cm ⁻¹	PNPRF-II Freq. cm ⁻¹	Assignment
3350	3353	H- Bonded Phenolic -OH
2928	2939	CH- Str.
1560, 1338	1560, 1338	Ar-NO ₂
1282, 902.8	*Res-CH ₂ -Res, CH-def
.....	992.8	*Pnp-CH ₂ -Pnp, CH- def.
933.7	933.7	Res-CH ₂ -Pnp, CH-def
833	831	1,2,3,4 tetra substituted aromatic ring
1221, 1089	1223, 1088	1,2,3,5 tetra substituted aromatic ring

*Res-Resorcinol, *Pnp-p-Nitrophenol

The broad bands at 3350 cm^{-1} and 3353 cm^{-1} was assigned to stretching vibration of hydrogen bonded phenolic group [12]. The absorption at 2928 cm^{-1} and 2939 cm^{-1} was assigned to $\text{-CH}_2\text{-}$ stretch shows the linkage of CH_2 in resin PNPRF [13]. The peaks at 1338 cm^{-1} and 1560 cm^{-1} was attributed to (N=O) for symmetrical and asymmetrical stretch respectively. The IR peaks at 1282 cm^{-1} , 902.8 cm^{-1} was attributed to CH-deformation in Res- CH_2 -Res moiety which was absent in PNPRF-II. Similarly the weak band at 992.8 cm^{-1} represents the CH deformation in pnp- CH_2 -pnp moiety.

This was not shown in IR spectra of PNPRF-I. The weak bands at 933.7 cm^{-1} was shown in the spectra of both resins which were assigned to the CH-deformation in Res- CH_2 -pnp moiety. Moreover the absorption at 833 cm^{-1} and 831 cm^{-1} in the spectra of PNPRF-I and PNPRF-II resins was attributed to 1,2,3,4 tetra substituted aromatic ring and the peaks at 1221 cm^{-1} , 1089 cm^{-1} for PNPRF-I and 1223 cm^{-1} , 1088 cm^{-1} for PNPRF-II was attributed to 1,2,3,5 tetra substituted aromatic ring [14].

2.3.3 ^1H NMR Spectra of PNPRF resins

^1H NMR spectra of terpolymeric resins using DMSO - d_6 solvent were scanned by BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh.

The ^1H NMR spectral data is tabulated in Table 4. The ^1H NMR spectra of PNPRF resins are shown in Figure 3 and Figure 4. The NMR characterization of resins was based on data available in literature [15]. The PNPRF-I and PNPRF-II terpolymer resin shows signals at 5.3 δ ppm and 5.1 δ ppm may be attributed to phenolic -OH (pnp-moiety). Signals at 4.9 δ ppm may be due to Phenolic (-OH) that is (res.moiety) in PNPRF-I resins. The signals at 7.1 δ ppm and 7.6 δ ppm may be due to aromatic proton in PNPRF-I and PNPRF-II terpolymeric resins. Signals at 3.7 δ ppm may be due to Res- CH_2 -Res in PNPRF-I resin. Signals at 2.5 δ ppm may be due to pnp- CH_2 -Res moiety in PNPRF resins. Signals at 2.07 δ ppm may be due to pnp- CH_2 -pnp moiety in PNPRF-II resin.

Table 4. ^1H -NMR data of PNPRF resins

PNPRF-I δ ppm	PNPRF-II δ ppm	Nature of proton assigned
3.7	Res- CH_2 -Res
2.5	2.5	Pnp- CH_2 -Res
....	2.07	Pnp- CH_2 -Pnp
7.1-8.2	7.6	Aromatic- H
5.3	5.1	Phenolic - OH (Pnp moiety)
4.9	Phenolic - OH (Res moiety)

2.3.4 UV-Vis spectra of PNPRF resins

UV-Vis spectra of terpolymer resins in DMSO Solvent recorded by UV-Vis Double Beam Spectrophotometer Shimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy, RTM Nagpur University, Nagpur.

The UV-Vis spectra data are given in Table 5. The UV-Vis spectra of PNPRF resins are shown in Figure 5.

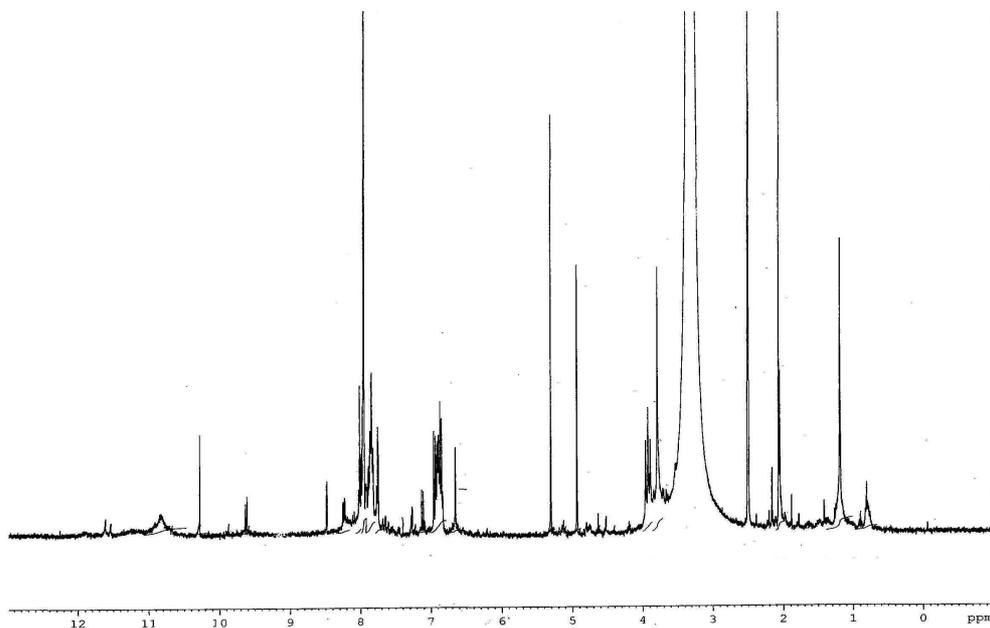


Figure 3: ¹H NMR spectra of PNPRF – I resin

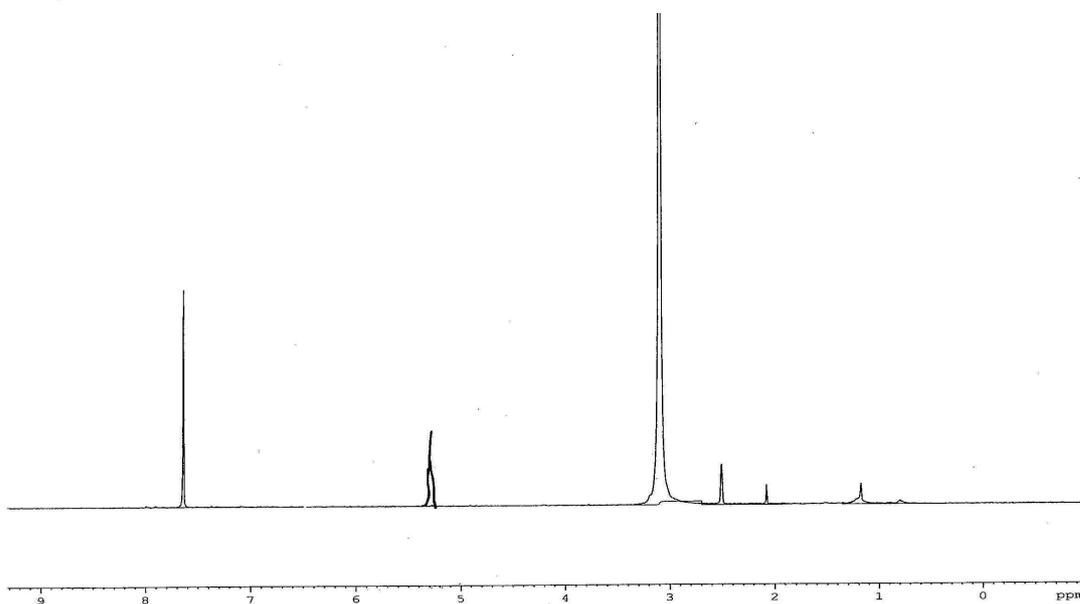


Figure 4: ¹H NMR spectra of PNPRF –II resin

Table 5. UV-Vis data of PNPRF resins

Resin	Wavelength, nm range for n- π^* transition	Wavelength, nm range for π - π^* transition	Group(moiety)
PNPRF-I	425	341	Pnp -NO ₂
PNPRF-II	433	328	Pnp -NO ₂

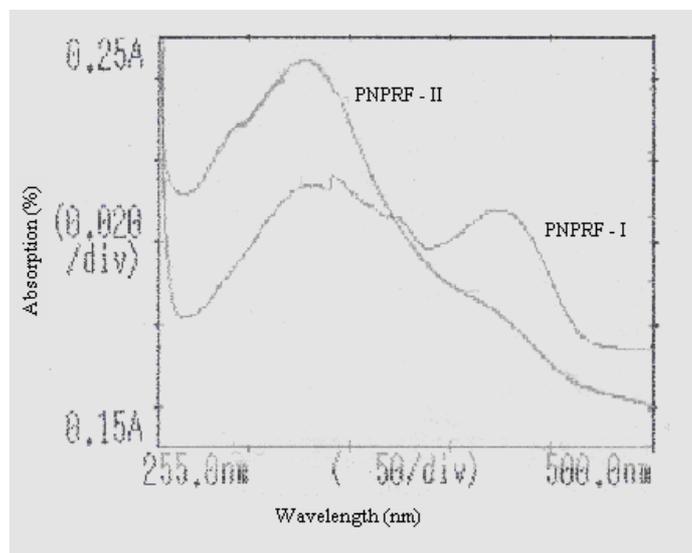


Figure 5: UV-Vis spectra of PNPRF resins

The band at 341 nm was due to NO₂ –group in conjugation with an aromatic nucleus and was characteristic of π - π^* transition while the band at 425 nm was assigned to n- π^* electronic transition in PNPRF-I resin. Similarly for PNPRF-II resin π - π^* and n- π^* transitions were found at 328 nm and 433 nm respectively [16, 17]. π - π^* transition shows hypsochromic shift while n- π^* transitions shows bathochromic shift in going from PNPRF-I to PNPRF-II (fig. 5).

2.4. Electrical conductivity of PNPRF resins

The DC conductivities of PNPRF resins were studied for temperature range 343 to 573K. The specific conductance of these resins was calculated from the values of specific resistance. The electrical conductivity as a function of temperature of the polymer was studied. The electrical conductance of polymeric materials depends upon incalculable parameters such as porosity, pressure, method of preparation and atmosphere. Generally polymers containing aromatic nuclei in the polymeric matrix exhibit lower activation energy than those with aliphatic system [18, 19]. The powdered samples of PNPRF resins were palletised by hydraulic press at pressure of 17 lb inch⁻². The surface of pallet were made conducting by applying graphite paste. The diameter and thickness was measured using screw gauge. The solid state conductivity as function of temperature was recorded by two probe method [20]. The electrical conductivity for PNPRF was found in the range of 0.0926 x 10⁻⁶ to 0.3294 x 10⁻⁶ mho cm⁻¹ and 0.0681 x 10⁻⁶ to 3.1316 x 10⁻⁶ mho cm⁻¹ for PNPRF-I and PNPRF-II resin. The plot of log σ versus 1/T was found to be linear in the temperature range under study, which indicate that the Wilson's exponential law, $\sigma = \sigma^0 \exp(-E_a/kT)$ was obeyed. Where, k=Boltzmann constant, σ =Electrical conductivity at temperature T, σ^0 = Electrical conductivity at temperature T $\rightarrow\infty$, E_a=Activation energy of conduction. The energy of activation (E_a) of electrical conduction calculated from the slopes of the plots was

found to be 4.089 kJmole⁻¹ and 5.365 kJmole⁻¹ for PNPRF-I and PNPRF-II resins respectively. Electrical conductivity plots of PNPRF resins are given in Figure 6. and Figure 7. Electrical conductivity data of PNPRF resins are shown in Table 6.

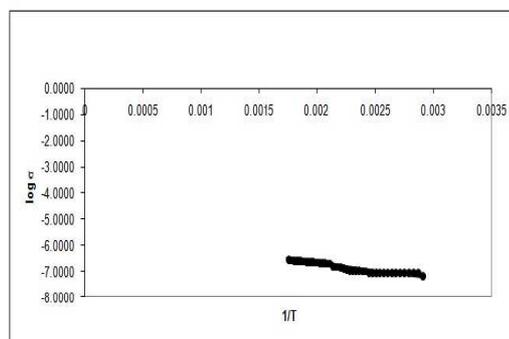
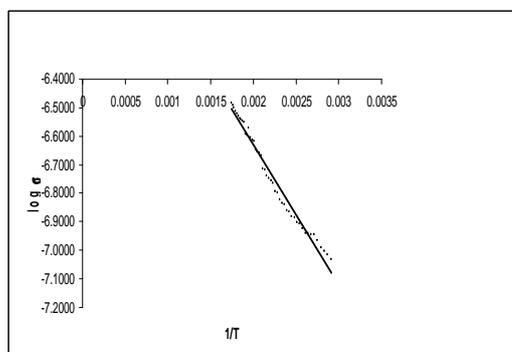


Figure 6:Electrical conductivity plot of PNPRF-I

Figure7:Electrical conductivity plot of PNPRF-II.

Table 6. Electrical conductivity data of PNPRF resins.

Resins	Temperature Range(K)	Activation energy (kJ mole ⁻¹)	Activation energy (eV) x 10 ²³
PNPRF-I	343-573	4.089	15.37
PNPRF-II		5.365	20.17

2.5. Antibacterial activity of PNPRF Resins

Antibacterial activities of resins were studied against gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and gram negative bacteria (*Escherichia coli*) at suitable concentration by Mueller Hinton Agar method [21]. DMSO system was used as control in this method. The inhibition zone was measured as diameter in four directions and expressed as mean. The results were compared using ampicillin (200µg/ml) a broad spectrum antibiotic as reference. Zone of inhibition (%) for resin samples are tabulated in Table 7.

Table 7. Antibacterial data of PNPRF resins

Resin	Zone of inhibition (%)								
	Gram+ve						Gram -ve		
	<i>B.subtilis</i>			<i>S. aureus</i>			<i>E. coli</i>		
Concentration (µg/ml)	200	400	600	200	400	600	200	400	600
PNPRF-I	47.1	52.9	72.34	1.54	17.93	25.43	44.76	62.16	74.26
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, FTIR spectra, ¹H NMR spectra, non aqueous conductometric titrations supports to the above tentative structures of PNPRF terpolymeric resins. Electrical conductivity of PNPRF terpolymeric resins increases by increasing temperature. Hence this terpolymer may be ranked as semiconductor. The activation energy of conduction of PNPRF-II is found to be higher than PNPRF-I. This conclude that as the mole

ratio of p-nitrophenol with respect to resorcinol is increased the conductivity decreases. This may be attributed to electron withdrawing nature of nitro group. This is in good agreement with the most probable structure proposed for the newly synthesised resin under investigation. Thus the low magnitude of activation energy of resin may be due to presence of large number of π -electrons in the polymer chain. Antibacterial activity results show good inhibition against gram +ve and gram -ve bacteria. The data suggest that all the samples are toxic to bacteria. PNPRF-I is good toxic to *B.substillis* than *S.aureus*. Similarly PNPRF-I shows good toxicity against gram -ve bacteria *E.coli* than PNPRF-II. Increase in nitro group as compared to phenolic -OH found to more toxic for gram -ve bacteria as compared to gram +ve.

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