

Synthesis and characterization of copolymer resin derived from phthalic acid and semicarbazide with formaldehyde.

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ABSTRACT

Copolymer (PTSF) has been synthesized using the monomers phthalic acid, semicarbazide and formaldehyde in 1:1:2 molar proportions. The structure of PTSF copolymer has been elucidated on the basis of elemental analysis and various physicochemical techniques, i.e. UV-Visible, FT-IR and ¹H-NMR spectroscopy. The number average molecular weights of resin were determined by conductometric titration in non-aqueous medium. Viscometric measurements in dimethyl formamide (DMF) have been carried out with a view to ascertain the characteristic functions and constants.

Keywords: Synthesis, polycondensation, resin, structure, degree of polymerization, Characterization.

INTRODUCTION

A literature survey reveals that copolymer derived from substituted hydroxy or dihydroxydithioamide - formaldehyde resin shows improved ion-exchange properties, thermal resistance property, coordinating property and good storage stability etc. [1]. Copolymers from 2-acrylamido-2-methyl propanesulfonic acid (APSA) and N-acryloyl-N-methyl piperazine (AP) were synthesized by radical polymerization have been reported in literature [2]. Salicylic acid-formaldehyde-resorcinol terpolymer resin was synthesized and its ion exchange capacity was measured. However, the literature studies have revealed that no copolymer has been synthesized using the monomer Phthalic acid, semicarbazide and formaldehyde.

Therefore, in the present communication we report the synthesis, structural characterization of PTSF copolymer. The elemental analysis has been carried out to ascertain the molecular formula and the spectral studies have been used to characterize the complete structure of the PTSF copolymer.

METHODOLOGY

MATERIALS

Pthallic acid (Ranbaxy Fine Chemicals, Mumbai) purified by rectified spirit. Formaldehyde (37%) (Qualigens Fine Chemicals, Mumbai) was used as received. Semicarbazide (Loba, Mumbai, extra pure) was used as received. The solvents and monomers were purified by the conventional methods [4].

SYNTHESIS

A mixture of phthalic acid [0.1mol], semicarbazide [0.1mol] and formaldehyde [0.2 mol] in the presence of 2M hydrochloric acid (200 ml) was heated in an oil bath at $126^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 6 h with occasional shaking [5-7]. The separated resinous product (PTSF) was washed with hot water to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitated by dropwise addition of 1:1 (v/v) HCl / water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions. The yield of the copolymer resin was found to be 80%. The reaction taking place is as shown in Fig.1.

ANALYTICAL STUDIES

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV-Visible studies were carried out using Shimadzu UV-1800 Spectrophotometer in the range 200-800 nm. The Infrared spectrum was recorded in the region of 500-4000 cm^{-1} on Shimadzu Affinity-1 FTIR Spectrophotometer, $^1\text{H-NMR}$ studied using Bruker Avance-II FT-NMR Spectrometer in DMSO-d_6 solvent. All the analytical and spectral studies for the newly synthesized copolymer were carried out at SAIF Punjab, Chandigarh.

RESULTS AND DISCUSSION

The copolymer resin (PTSF) sample was white in color, insoluble in commonly used organic solvents but were soluble in DMF, THF, DMSO, Conc. HCl and aq. NaOH. No precipitation and degradation occurs of resin in all the solvents. These resins were analyzed for carbon, hydrogen and nitrogen content. The resin synthesized do not show sharp melting point but undergo decomposition above 300°C . This resin was then purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value, as-
Calculated for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_5$: C: 49.81 % ; H: 4.15 % ; N: 15.84 %., O: 30.18%,
Found for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_5$: C: 50.02 % ; H: 4.34 % ; N: 15.06 %., O: 30.90%,

CHARACTERIZATION OF COPOLYMER

Molecular weight of copolymer was determined by non-aqueous conductometric titration. The number average molecular weight (\overline{Mn}) could be obtained by multiplying the (\overline{Dp}) by the formula weight of the repeating unit [8]. The result of the molecular weight of copolymer samples prepared using higher proportion of two monomers (Pthalic acid and Semicarbazide) has the highest molecular weight in the series. The molecular weight for PTSF is 1373.49 (Fig.2.).

The molecular weight (\overline{Mn}) of the copolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in 50% (v/v) DMF/ alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of copolymers was made. Inspection of such a plot revealed that there are many breaks in plot. From this plot the first break and the last break 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 the more acidic phenolic hydroxy group of all the repeating units; and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxy group of all

repeating units are neutralized. On the basis of the average degree of polymerization (\overline{Dp}) is given by the following relation- Total meq. of base required for complete neutralization i.e. last break. Meq. of base required for smallest interval i.e. first break. The number average molecular weight (\overline{Mn}) could be obtained by multiplying the (\overline{Dp}) by the formula weight of the repeating unit [9]. The results are incorporated in Table-1.

Specific Conductance = Observed Conductance × Cell Constant

$$\overline{Dp} = \frac{\text{Total meq. of base required for complete neutralization}}{\text{Meq. of base required for smallest interval}}$$

$$\overline{Mn} = \overline{Dp} \times \text{Repeat unit weight}$$

Viscometric measurements were carried out in DMF at six different concentration ranging from 3.0 % to 0.5 % in 23 °C with precession of ± 0.1 °C. The resin showed normal behaviour. The intrinsic Intrinsic viscosities [η] were calculated by the Huggin's (1) equation and Kraemmer's, (2) equation which are given below. The viscometric plots are shown in Fig.-2. In accordance with the above relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were found to be linear giving as slopes K_1 and K_2 respectively. The intercept on the axis of viscosity function gave the [η] value in both the plots. The calculated values of constants K_1 and K_2 [Table-1] in most of cases satisfy the relation. $K_1 + K_2 = 0.5$ favourably. The values of [η] obtained from equation (1) and equation (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of copolymer.

$$\eta_{red} = \eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \tag{1}$$

$$\ln \eta_{rel}/C = [\eta] - K_2 [\eta]^2 C \tag{2}$$

Where,

η_{sp} = Specific viscosity, this function has been derived from relative viscosity and given by

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_{rel} - 1.$$

η_{red} = Reduced viscosity

η_{rel} = Ratio between viscosity of solution (η) and viscosity of the solvent (η_0) is known as relative viscosity,

[η] = As the reduced viscosity (η_{red}) is dependent on the concentration of polymer sample, it is necessary to extrapolate a plot of reduced viscosity against polymer concentration (C) to zero concentration, to get intrinsic viscosity which is characteristics parameter of a polymer.

Hence intrinsic viscosity is given as

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/C).$$

C = Concentration in gm/100ml.

K_1 = Huggin's constant

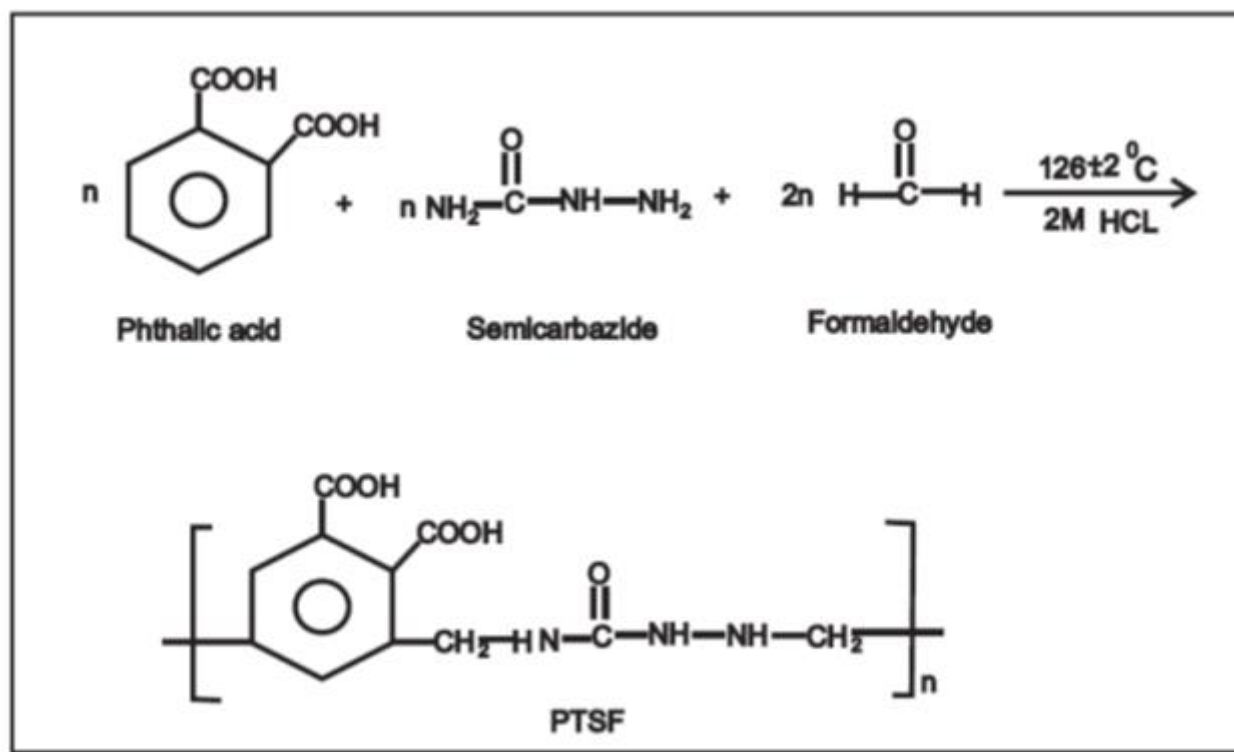
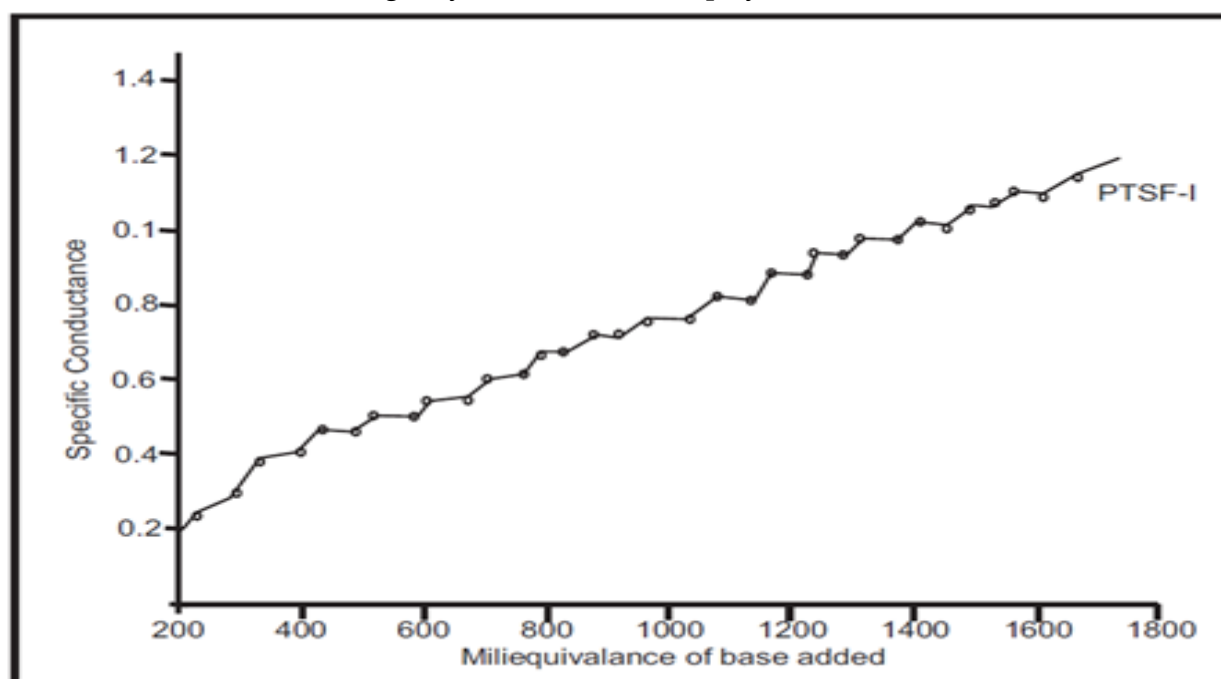
K_2 = Kraemmer's constant

The electronic spectra of the PTMF copolymer resin is shown in Fig.4. UV-visible spectra of all the purified copolymer has been recorded in pure DMF. The perusal of the UV-visible spectra of copolymer showed almost similar nature. The spectra of the copolymer shows two bands in the region 240 to 270 nm and 330 to 340 nm. The observed positions of the absorption bands with different intensities indicate the more intense band 260 nm is due to ($\pi \rightarrow \pi^*$) allowed transition of pthallic acid moiety which readily attains coplanarity and shoulder merging (loss of fine structure) and also due to chromophore groups like $>C=C$ groups are in conjugation with an aromatic nucleus (aromatic ring) and the less intense band at 334 nm may be due to ($n \rightarrow \pi^*$) forbidden transition in $>C=N$, $-C=O$ and $-OH$ groups [10].

The IR spectra of copolymer resin is presented in Fig.-5. The IR spectra revealed that the resin give rise to a broad band appearing in the region 3400-3800 cm^{-1} may be assigned to the stretching vibration of carboxylic acid groups exhibiting intermolecular hydrogen bonding. The band at 2900 cm^{-1} assignable to $-NH-$ stretching, bending and deformation out of plane vibrations of melamine moiety in copolymers respectively. The band at 1502 cm^{-1} may be ascribed to aromatic skeletal ring. The presence of methylene bridges ($-CH_2-$) in the polymeric chain may be assigned due to presence of band at 1460-1470 cm^{-1} , 1375-1360 cm^{-1} and 788-753 cm^{-1} [11-12]. [$-CH_2-$ rocking] .

Table: 1

Copolymer	Empirical formula repeating unit	Empirical formula weight	(\overline{Dp})	(\overline{Mn})	Intrinsic viscosity dl g ⁻¹	Huggin's Constant (K ₁)	Kraemer's Constant (K ₂)	K ₁ + K ₂
PTSF	C ₁₁ H ₁₁ N ₃ O ₅	265	7.27	1373.49	0.72	0.1067	0.48794	0.594

**Fig.1. Synthesis of PTMF Copolymer Resin****Fig.2. Conductometric Titration Data for PTSF copolymer Resin**

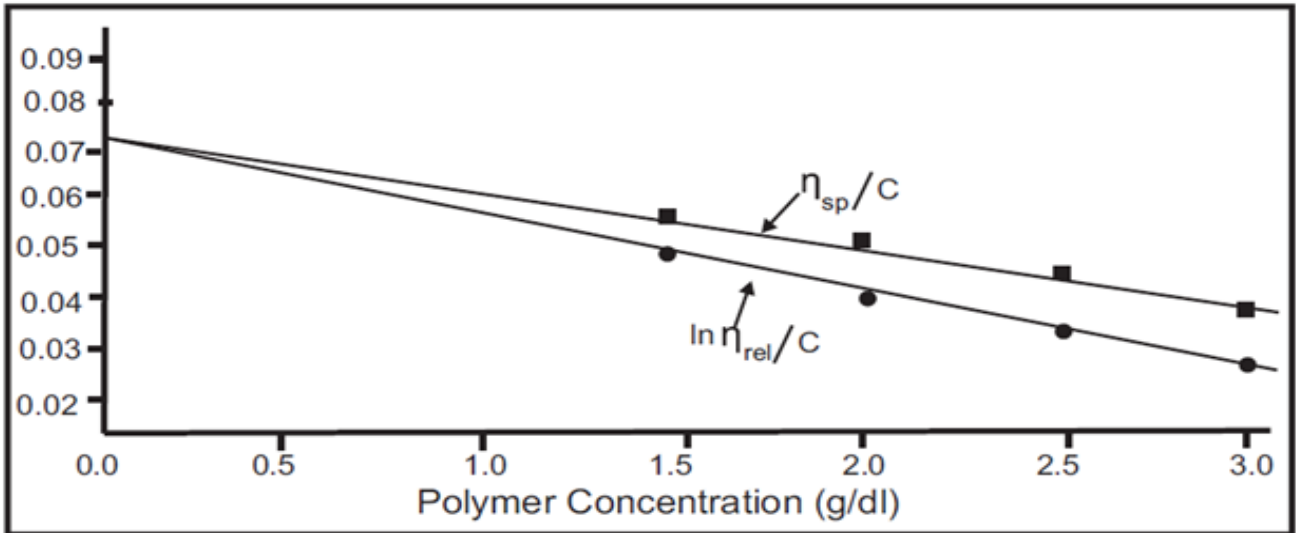


Fig. 3. Viscometric Plots of PTSF Copolymer Resins

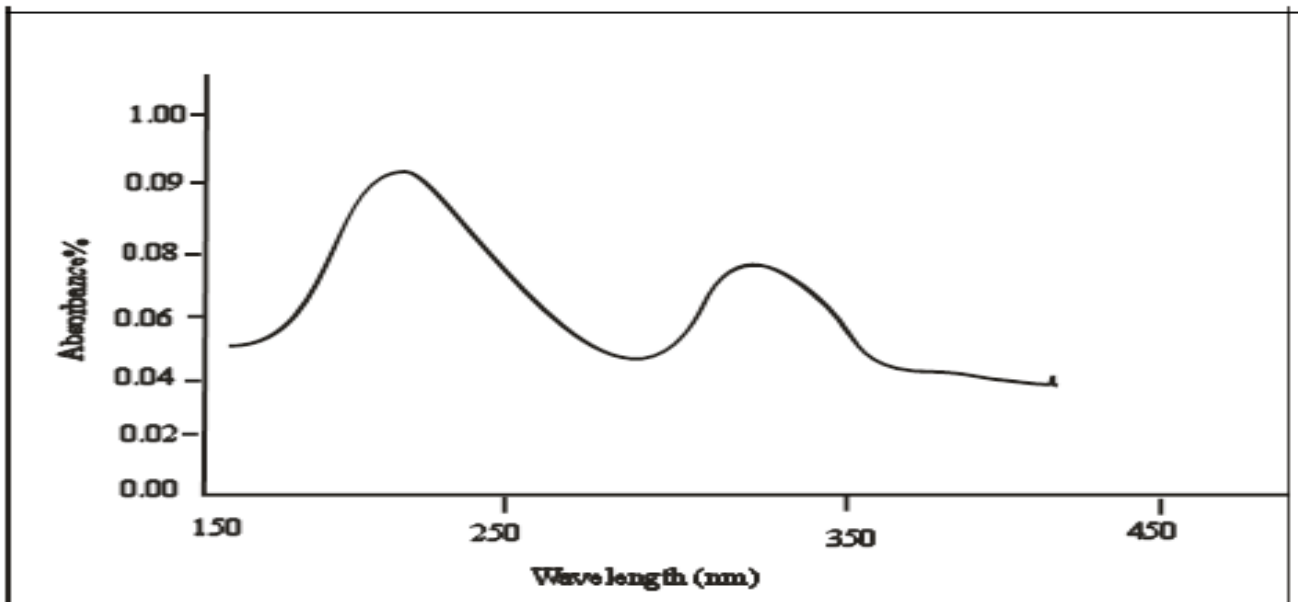


Fig. 4. UV-Visible Spectra of PTSF Copolymer Resin
RC SAIF PU, Chandigarh

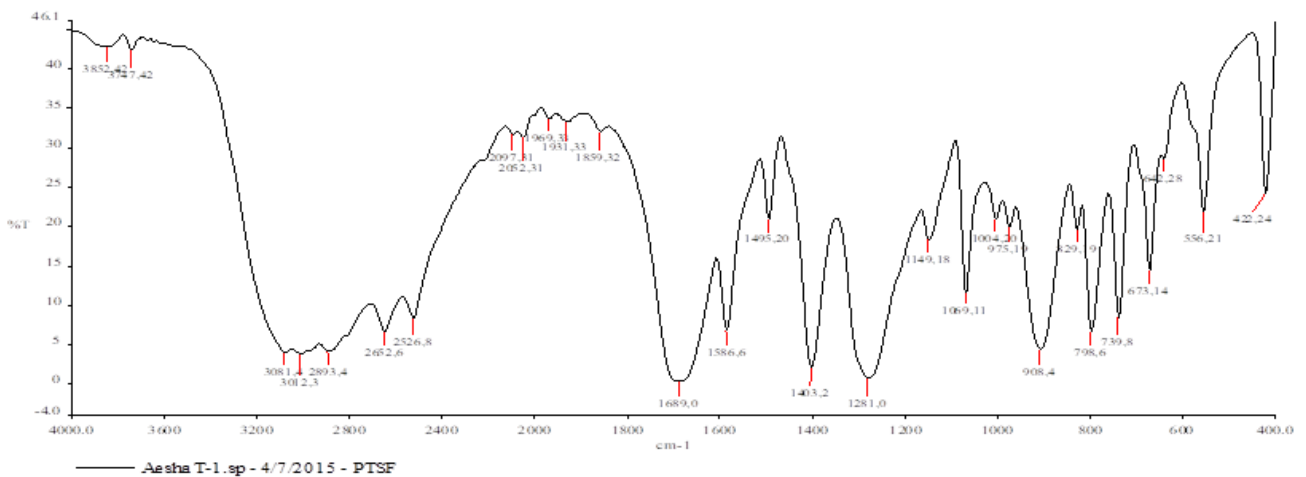


Fig.-5: Infrared spectra of PTSF copolymer

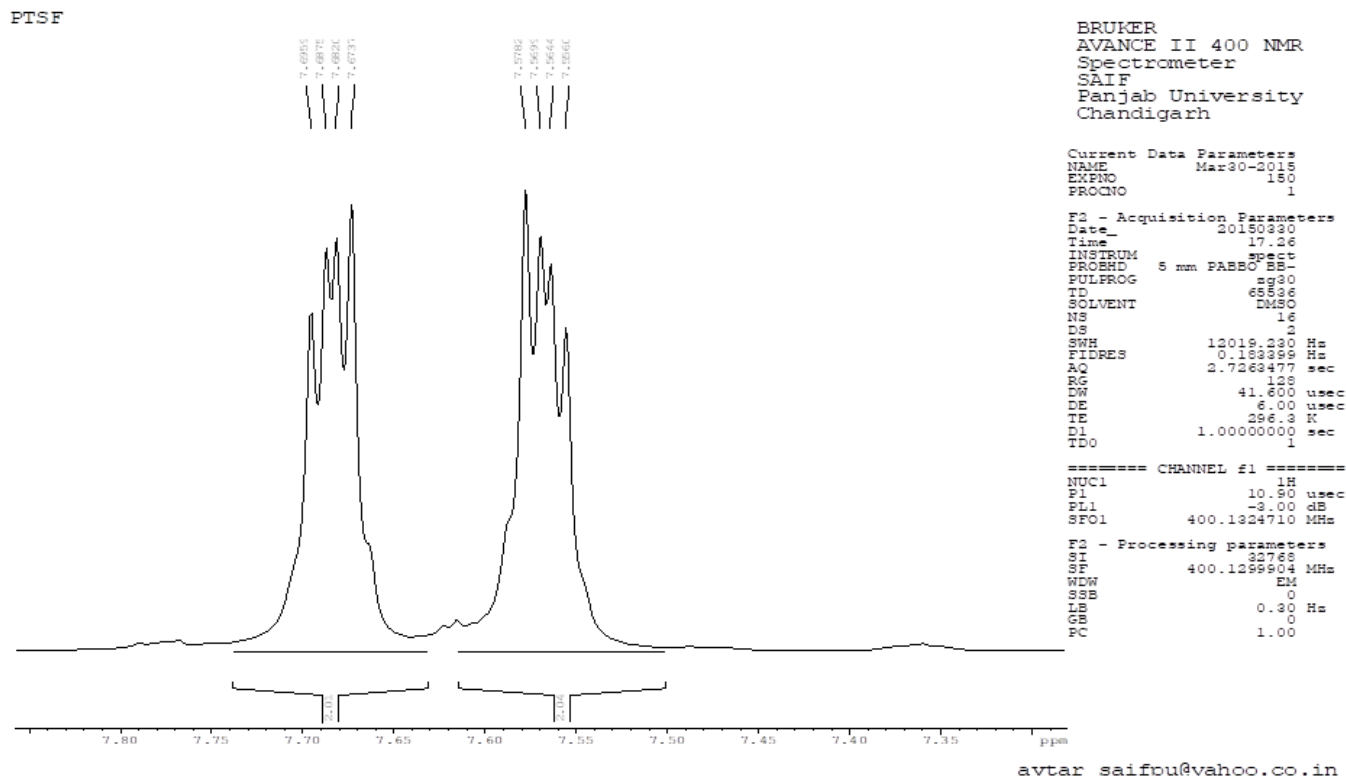


Fig. 6. ^1H -NMR Spectra of PTSF Copolymer Resin

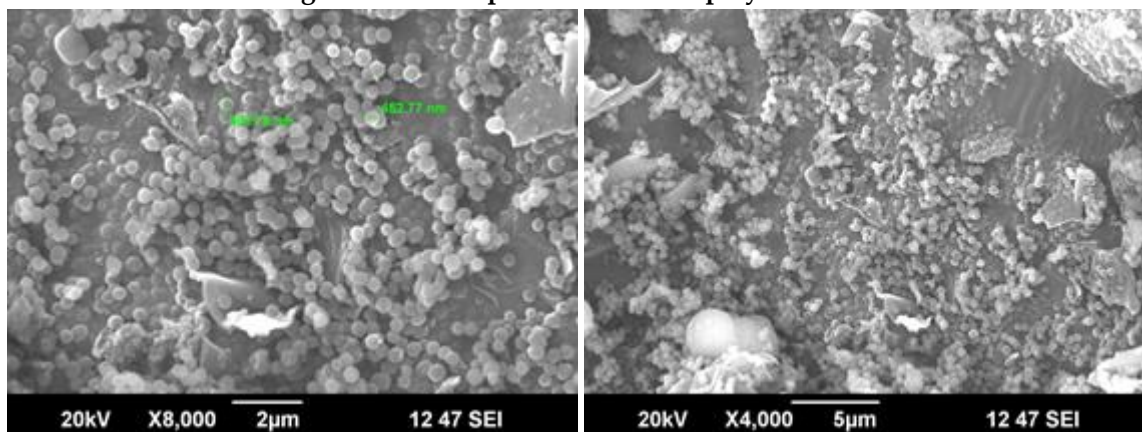


Fig.7. Scanning Electron Microscopy Images of PTSF Copolymer Resin

^1H NMR spectra of copolymer resin is presented in Fig.6. ^1H NMR spectra of copolymer resin show the intense signal arising in the region 7.6959(δ) ppm which may occur on account of hydroxyl proton of -COOH group involved in the intermolecular hydrogen bonding[13-14]. The sharp intense peak at 7.6875(δ) ppm may be assigned to aromatic proton. A weak signal made its appearance at 7.6820 (δ) ppm which may be due to amido protons of -NH bridge in the chain. An intense signal appearing at 7.5560 (δ) ppm may be due to methylene proton (-CH₂-). Copolymer show signal around 7.5644 (δ) ppm suggesting the presence of methylene bridges of Ar-

CH₂-N linkage. NMR spectra of all PTSF copolymer resins are taken in DMSO-*d*₆ solvent. The spectra are presented in Figure and the spectral data are given in Table.

Surface analysis has found great use in understanding the surface features of the materials. The morphology obtained in different magnifications for the PTSF copolymer resin was investigated by scanning electron micrographs are shown in Fig.7. It gives the information of surface topography and defect in the structure. It indicates that the PTSF copolymer has a net-like appearance and the surface features of the

copolymer shows a fringed, scattered, spherulites and miscellaneous model of the crystalline-amorphous structure. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of PTSF copolymer resin sample.

Scanning electron microscopy of copolymer was carried out to understand the inner morphology and pore structure. The morphology of fracture surfaces of the copolymer is quite different from that of polymer-metal complexes. It is clear from SEM that the copolymer is porous in nature. The morphology of the copolymer shows a fringed model of the semicrystalline nature. The fringes represent the transition between the crystalline and the amorphous phases. The copolymer exhibits a more amorphous character with a close-packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix. The presence of few holes and cracks are noted which may be due to air voids [15].

The PTSF copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity. The polymer under study is copolymer and hence, it is very difficult to assign their exact structures. On the basis of the nature and reactive, position of the monomer, elemental analysis, electronic, FT-IR, ^1H NMR, spectra, SEM and molecular weight, the most probable structures have been proposed for copolymer resin.

Conflicts of interest: The authors stated that no conflicts of interest.

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