



ION EXCHANGE PROPERTIES OF COPOLYMER RESIN DERIVED FROM PHTHALIC ACID, THIOSEMICARBAZIDE AND FORMALDEHYDE

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ABSTRACT:

A novel chelating terpolymer resin has been synthesized through the copolymerization of phthalic acid and thiosemicarbazide with formaldehyde in 2:1:3 mole ratio using hydrochloric acid as a reaction medium by condensation technique. The synthesized copolymer resin was characterized by UV-visible, FTIR, proton NMR spectroscopy. On basis of the spectral studies, the structure of the copolymer resin was proposed. The physico-chemical parameters have been evaluated for the copolymer resin. Non-aqueous conductometric titration was used to determine the average molecular weight and polydispersity of the PTF-II copolymer resin and the intrinsic viscosity was also determined. The semicrystalline nature of the synthesized copolymer was established by scanning electron microscopy (SEM). Copolymer synthesized is proved to be selective chelating ion exchange copolymer resin for certain metals. chelating ion exchange properties of this polymer was studied for Fe³⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺ and Pb²⁺ ions. A batch equilibrium method was employed in the study of the selectivity of the distribution of a given metal ions between the polymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in a media of various ionic strengths.

Keywords :- Synthesis, Condensation, characterization, structure, viscosity, ion exchange.

INTRODUCTION :

Currently industrial pollution is major concern because of industrial waste includes heavy metals, often contained in the wastewater. When these metals release into the environment can cause severe damage to the human body, including accumulative poison, brain damage, and cancer [1]. Several processes were accessible for heavy metal removal, including chemical precipitation, membrane, and retention technique [2]. Ion-exchange process was found to be an effective technique to separate the selective metal ions from wastes. Ion-exchange resins are polymers that can reversibly interchange the counter ions. The resins are organized into two main types depending upon the charge of the counter ions with which they can exchange. The cationic exchangers which interchange the positively charged ion and the anionic exchange resin

interchanges the negatively charged ion due to the existence of the positively ionisable group. Polymeric resin was synthesized and reported for its ion-exchange characteristics towards selective metal ions. Ion-exchanger may be defined as the reversible exchange of ions between the substrate and medium. Many copolymers are now being synthesized with reactive groups, tested and used not only for the macromolecular properties but also for the properties of functional groups. These functional groups provide an approach to a subsequent modification of the copolymers for specific end application. The literature survey reveals that Khobragade and co-workers studied the interaction of heavy metal ions and chelating ion-exchange resin containing phthalic acid [3]. The resin has good selectivity to exchangeable adsorption of heavy metal ions indicating Cu (II), Hg (II), Pb (II) and Mg (II) at

pH 5.0 and also suggested that the chelating ion-exchange resin containing phthalic acid could be used to enrich heavy metals in water and their analysis. The polymeric materials were used for transition metal ion adsorption and desorption of selected ions Cu (II), Ni (II), Co (II), Cd (II), and Pb (II) from aqueous media containing different amounts of these metal ions at different pH values. The adsorption rates were high and the adsorption equilibrium was reached in about 30 min. The affinity order of the transition metal ions was Cu (II) > Ni (II) > Co (II) > Cd (II) > Pb (II) for competitive adsorption. Gurnule and co-workers have prepared 8-hydroxyquinoline-5-sulphonic acid-Thiosemicarbazide-Formaldehyde [4]. The chelating ion-exchange properties of this were studied for Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺, Fe³⁺ and Pb²⁺ ions. A batch equilibrium method was used to study the selectivity of metal ion uptake by measuring the distribution of a metal ion between the resin sample and solution containing the metal ion. The study was carried out at different pH ranges and in medium of different ionic strengths. The copolymer showed higher selectivity for Fe (III), Cu (II) and Ni (II) ions than Co (II), Zn (II), Cd (II) and Pb (II) ions.

EXPERIMENTAL :

All the materials and chemicals (Aldrich, USA) were used as received with analytical grade.

Synthesis of Phthalic acid – Thiosemicarbazide – Formaldehyde (PTF-II) terpolymer in 2:1:3 Mole Ratio.

A collective mixture of phthalic acid (3.32g, 0.2mol) and thiosemicarbazide (0.911 g 0.1mol) with formaldehyde (11.25 ml, 0.3mol) was taken as monomers in a clean round bottom flask equipped with mechanical stirrer and a refluxed condenser using 2M hydrochloric acid (200 ml) as a reaction medium in 2:1:3 mole ratios. The homogeneous mixture was refluxed in an oil bath at 126 ± 2 °C with constant stirring for 5 h. After the reaction time was over, the resultant

mixture was cooled and then poured into crushed ice with vigorous shaking. The product was neutralized by 8% aqueous NaOH and 1:1 HCl/Water under ice cold condition to remove the impurities from the terpolymer. This re-precipitation technique was repeated thrice. Finally the terpolymer was thoroughly washed with warm water, methanol and ether and filtered off. The filtered terpolymer was dried in oven at 75°C for 24 h. The dried resin was powdered well and sieved into uniform size using the mesh screen. The yield of the terpolymer was found to be about 84%

II Copolymer Resin

Instruments

The copolymer resin (PTF-II) sample was white in color, soluble in solvents such as DMF, DMSO and CDCl₃ while insoluble in almost all other organic solvents. These resins were analyzed for carbon, hydrogen and nitrogen content. The resin synthesized do not show sharp melting points but were found to be in the range of 480K – 485K. 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 C₂₀H₁₇N₃S O₈ : : C: 46.97 % ; H: 3.91 % ; N: 14.94 % , S:11.38%, O: 22.77%,

Found for C₂₀H₁₇N₃S O₈ : : C: 46.52 % ; H: 3.15 % ; N: 14.49 % , S:11.02%, O: 22.30%.

By using Tuan-Fuoss viscometer viscosities were determined at six different (concentration ranging from 3.0 wt % to 0.5 wt % of resin in DMF at 33°C. The intrinsic viscosity was calculated by the Huggins equation (1) and Kramer equation (2)

Where, η_{sp} = Specific viscosity, this function has been derived from relative

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

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

$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \dots\dots\dots(1)$$

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

The reduced viscosity η_{red} of the copolymer resin samples were calculated by the formula η_{sp}/C . Reduced viscosity versus concentration was plotted for each set of data. The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots. According to the above relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were linear with slopes of K_1 and K_2 , respectively. Intercepts on the viscosity function axis gave $[\eta]$ value in both plots. The calculated values of the constants K_1 and K_2 in most cases satisfy the relation $K_1 + K_2 = 0.05$ favourably. The intrinsic viscosity values obtained from both the plots have been found to be in close agreement with each other. It is observed that, the intrinsic viscosity value increases with the increases in molecular weight of terpolymer [5-6]. Solvent - DMSO, Efflux time of pure solvent to = 220 Sec., Temperature = 32° C = 305K

The molecular weight (M_n) of the copolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in 50% (v/v) DMF/ alcohol mixture using 50 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 50 mg of copolymers was made. There are many breaks in plot. From this plot the first break and the last break were noted in Fig. The calculation of (M_n) by this method is based on the following considerations.

(1) The first break corresponds to neutralization of the more acidic carboxylic 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 carboxylic group of all repeating units are neutralized. On the basis of the average degree

of polymerization (D_p) is given by the following relation-

$$\text{Specific Conductance} = \frac{\text{Observed Conductance} \times \text{Cell Constant}}{D_p}$$

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

$$\overline{M_n} = \overline{D_p} \times \text{Repeat unit weight}$$

Spectral Analysis

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV-Visible studies were out carried using Scimadzu 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.

Electronic spectra

The UV-visible spectra of PTF-II copolymer in pure DMF were recorded (Figure 4). The perusal of the UV-visible spectra of copolymers showed almost similar nature. The spectra of these copolymers exhibit two absorption maxima in the region 230-260 nm and 330 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) having a carbon-oxygen double bond which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The shift from the basic value (viz. 260 nm and 330 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ϵ_{max} higher values [7-9].

IR spectra

The FTIR spectra of PTF-II copolymer resin are depicted in Figure 5. The terpolymer spectrum

showed a broad band in the region 3460 cm^{-1} may be assigned to the hydroxyl group of $-\text{COOH}$ present in the aromatic ring. A band appeared at 2945 cm^{-1} is assigned to aromatic ring ($-\text{CH}$) stretching modes. The 1,2,3,5 tetra substitution of aromatic benzene ring is confirmed by the bands appeared between 1266 cm^{-1} and 728.04 cm^{-1} [15]. The band appeared at 1724.40 cm^{-1} is assigned to $-\text{C}=\text{O}$ stretching vibrations of $\text{Ar}-\text{COOH}$ [10]. The band appeared in the region of 1433.01 cm^{-1} to 1266 cm^{-1} is attributed to $-\text{CH}_2$ - bending (twisting & wagging) mode of vibrations [11]. The presence of $-\text{NH}$ bridge may be due to the band appeared at nearly 2995 cm^{-1} . The band displayed at 1650 cm^{-1} may be due to stretching vibration of $-\text{C}=\text{S}$.

Nuclear magnetic resonance spectra

^1H NMR spectrum of PTF-II copolymer is shown in Figure 5 and the NMR spectra of PTF-II copolymer resin was scanned in $\text{DMSO}-d_6$ solvent. The weak multiple signal (unsaturated pattern) in the region 8.22 to 8.30 (δ) ppm that is due to aromatic protons. Weak signal in the range of appeared in the range at 10.32 to 10.62 (δ) ppm may be due to the proton of $\text{CO}(\text{OH})$ in $\text{Ar}-\text{COOH}$. The much downfield chemical shift for aromatic carboxyl $-\text{OH}$ indicates clearly the intramolecular hydrogen bonding of $-\text{OH}$ group [12-15]. Triplet signal appeared in the region 5.35 (δ) ppm can be assigned to amine proton of $-\text{C}-\text{NH}-\text{C}-$ linkage. Intense signal appeared in the region 3.98 to 4.30 (δ) ppm may be due to protons of methylenic bridges (CH_2) of polymer chain.

Scanning Electron Microscopy (SEM)

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning electron micrographs at different magnification, which are shown in Figure 6. It gives the information of surface topology and defect in the structure.

The resin appeared to be dark brown in colour. The morphology of copolymer resin shows spherulites and fringed model. The spherulites are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of PTF-II copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous, when compare to the other resin [16], the PTF-II copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

ION-EXCHANGE STUDIES OF COPOLYMER RESINS

The ion-exchange capacity for the synthesized copolymer resins was determined by batch equilibrium method developed by Gregor and Degeiso et al.

Procedure

The finely powdered terpolymer was used to determine its ion-exchange capacity for specific metal ions such as Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+} in the form of their aqueous metal nitrate solutions rather chlorides or sulphates in order to avoid the precipitation of the chosen metal ions. Chelation ion-exchange characteristics of the copolymers were studied to assess the effectiveness of the terpolymer to exchange the cation under the following changing experimental conditions [17-19].

Preparation of standard solutions

a) **Electrolyte solutions:** 1 M of stock solutions of electrolytes such as NaCl , NaNO_3 , Na_2SO_4 and NaClO_4 has been prepared. From the stock solution of each electrolyte, different concentrations *viz.* 0.01, 0.1 and 0.5 M of solutions were prepared using double distilled water.

b) **Metal nitrate solutions:** 0.1 M of standard solution has been prepared for the chosen metal nitrate *viz.* Ferric nitrate, Cobalt nitrate, Nickel nitrate, Copper nitrate, Zinc nitrate and Lead nitrate using double distilled water.

c) **EDTA solution:** 0.1 M of disodium salt of EDTA was used as the standard solution for the complexometric solution.

ij) Evaluation of metal ion uptake capacity in the presence of various electrolytes in different concentrations

The terpolymer (25 mg) was taken in a pre-cleaned glass bottles and each of the electrolytes (25 mL) such as NaCl, NaNO₃, NaClO₄, and Na₂SO₄ in different concentrations *viz.* 0.01, 0.1, and 0.5 M were added into the bottles. The pH of the suspension was adjusted to 2.5 for Fe³⁺, pH 4.5 for Cu²⁺ and Ni²⁺, pH 5.0 for Co²⁺ and Zn²⁺ and pH 6 for Pb²⁺ either by adding 0.1M HCl or 0.1M NaOH. The suspension was mechanically stirred for 24 h at room temperature. After 24 h, 0.1M of the chosen metal ion solution (2 mL) was added to each bottles and again vigorously stirred at room temperature for 24 h. The terpolymer was then filtered off and washed with distilled water. The filtrate and the washings were collected and then the amount of metal ion was estimated by titrating against standard Na₂EDTA solution using appropriate indicator. A blank experiment was also performed following the same procedure without the terpolymer sample. The amount of metal ions taken up by the terpolymer in the presence of a given electrolyte can be calculated from the difference between the actual titrate value and that of from the blank. The uptake of metal ions by the terpolymer resin was calculated using the formula and expressed in milli mol/g .

Metal ion uptake by the terpolymer resin = (X-Y)Z milli mol/g (1)

where, 'Z' mL is the difference between the actual experimental reading and blank reading. 'X'g of metal ion in the 2 mL 0.1 M metal nitrate solution. 'Y'g of metal ion in the 2 mL 0.1 M metal nitrate solution after uptake. The above experiment was performed for all the chosen metal nitrate solution in the presence of four different electrolytes with three different concentrations.

ii) Evaluation of the distribution of metal ion uptake at different pH ranges

About 25 mg of the copolymer was stirred in 1 M NaNO₃ solution (25 mL) at required pH value for 24 hours at room temperature. To the swelled polymer 0.1 M metal ion solution (2 mL) was added and the pH was adjusted to the required value by adding either 0.1 M HCl or 0.1 M NaOH. The mixture was again mechanically stirred for 24 hours. The experiments were carried out with pH ranging from 1.5 to 6 for Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺ and Pb²⁺. In case of Fe³⁺ the study was carried out from pH 1.5 to 3.0 in order to avoid the precipitation. After 24 hours, the mixture was filtered, the filtrates and washing were collected. The amount of the metal ion which remained in the aqueous phase was estimated by the titration with standard EDTA solution using suitable indicator. Similarly blank experiment was carried out without adding the terpolymer. The amount of metal adsorbed by the terpolymer was calculated from the difference between the sample and blank reading. If the original metal ion concentration is known and the metal ion adsorbed by the polymers were estimated. The general expression for the distribution ratio K_d is as follows

$$D = \frac{\text{Amount of metal ion in solution} \times \text{Volume of solution (ml)}}{\text{Amount of metal ion on resin} \times \text{Weight of resin (g)}}$$

Metal ion adsorbed (uptake) by the resin = (ZX/Y) x (2/0.025)

Where, 'Z' = is the difference between actual experiment reading and blank reading,

'X' = gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,

'Y' = gm of metal ion in 2ml of metal nitrate solution after uptake.

iii) Evaluation of rate of metal ion uptake at different time intervals

Evaluation of the rate of metal ion taken by the copolymers was carried out by

measuring the time required for attaining the state of equilibrium between the polymer and metal ion under the experimental conditions. A series of experiments

were carried out to determine the amount of metal ion adsorbed by the terpolymer from time to time (1, 2, 3, 4, 5, 6...24 h) at room temperature. 25 mg of the polymer

sample was mechanically stirred with 25 mL of 1 M NaNO₃ and the pH of the suspension was adjusted to the required value by adding either 0.1 M HCl or 0.1 M

NaOH. It is assumed that under the given experimental conditions the state of equilibrium is established within 24 hours at room temperature. After the stipulated time, the suspension was filtered and washed with the distilled water. The filtrate was collected and the unadsorbed metal was estimated by titration with standard EDTA solution using appropriate indicator. From the difference between the original amount of metal added at the beginning of the experiment and the amount of unadsorbed metal ion, the amount of metal ion adsorbed by the polymer after specific time interval was calculated. The rate of metal ion uptake is expressed as the percentage of the metal ion taken up after a specified time interval related to that in the state of equilibrium as given as,

$$\text{Metal ion uptake} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

Using the following calculation, the rate of metal ion uptake was calculated. 'X'

g of metal ion adsorbed after 1 hour and 'Y' g of metal ion is adsorbed after 24 hours, then the percentage of metal ion adsorbed after 1 hour will be $(X / Y) \times 100$.

Ion-exchange capacity

The term ion exchange capacity is intended to describe the total available exchange capacity of a resin, as described by the number of functional group on it. Ion exchange capacity was determined by following experimental procedure[20-22]. 25 mg of the terpolymer resin sample was suspended in 50 mL of double distilled water. To this, 25 mL of 0.5 M sodium acetate solution was added. The mixture was stirred for 2 to 5 min. when H⁺ ions from the resin liberated in the solution to form acetic acid and adsorbed sodium ion (Na⁺). Then the solution was filtered and the filtered is titrated with 0.5 M NaOH solution. The ion-exchange capacity can be calculated by the following equation in milli mole per gram. (mili mol.g-1)

$$\text{Ion-exchange capacity of terpolymer resin} = XY / Z \dots\dots\dots (31)$$

where, X = molarity of NaOH, Y = volume of NaOH required during titration

Z = weight of the ion-exchanger. The ion-exchange capacity of the terpolymer resin has been determined and compared with the commercial ion-exchangers.

D = Weight (mg.) of metal ion taken up by 1 gm. of copolymer/ Weight (mg.) of metal ions present in 1 ml. of solution.

[M(NO₃)₂] = 0.1 mol./lit.; Volume of metal solution = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs (equilibrium state), at room temperature.

Weight of resin = 25 mg; Time = 24 hrs, at room temperature.

Metal ion uptake = (amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium.

CONCLUSIONS :

PTF-II resin was prepared from phthalic acid and Thiosemicarbazide with formaldehyde in hydrochloride acidic medium by condensation technique. The semi crystalline nature of the PTF-II copolymer resins were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{3+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} ions. The PTF-II copolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. The copolymer showed a higher selectivity for Cu^{2+} and Fe^{3+} ions than for Co^{2+} , Ni^{2+} and Zn^{2+} ions.

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Table: 1. Viscosity and Molecular Weight of PTF-II Terpolymer Resins.

Copolymer	Intrinsic Viscosity	K1	K2	K1+K2
PTF-II	0.12	0.4134	-0.2233	0.6367

Table.2 . Number Average Molecular Weight of PTF-II Copolymer by Conductometric Titration.

Terpolymer	First stage of neutralization (meq/100 g of terpolymer)	Final stage of neutralization (meq/100 g of terpolymer)	Degree of polymerization (\overline{DP})	Number average molecular weight (\overline{Mn})
PTF-II	155	1120	9.07	3400

Table 1. Distribution ratio D of various metal ion as a function of the pH by PTF-II copolymer resin.

Metal ion	Distribution ratio of metal ion at different Ph									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe ³⁺	112.4	128.9	146.9	387.6	-	-	-	-	-	-
Cu ²⁺	-	-	-	42.09	56.79	61.77	72.72	96.29	146.33	192.62-
Cd ²⁺	-	-	-	56.92	64.50	167.08	207.41	168.76	254.34	284.36
Zn ²⁺	-	-	-	76.7	124.83	188.55	268.67	466.67	419.05	544.14
Ni ²⁺	-	-	-	38.30	44.009	68.136	92.52	72.72	114.64	326.34
Pb ²⁺	-	-	-	72.36	84.05	144.59	378.95	684.06	1428.3	2466.1

Table 2. Comparison of the rates of metal (M) ion uptake by PTF-II copolymer resin

Metal ion	% of metal ion uptake at different time (hrs.)					
	1	2	3	4	5	6
Fe ³⁺	62.6	85.2	105.6	-	-	-
Cu ²⁺	15	25	38	45	55	62.7
Cd ²⁺	19.2	28	46	52	58.2	68.5
Zn ²⁺	38	46	56	65	68.5	88.5
Ni ²⁺	6	14	28	34.4	48	52.4
Pb ²⁺	42	54	68	78	88	90

Table. 3. Evaluation of the effect of different electrolytes on the uptake of several metal ions by PTF-II resin.

Metal ion	Electrolyte (mol./l)	pH	Weight of metal ion (in mg. ⁻¹) taken up in the presence of			
			NaClO ₄	NaCl	NaNO ₃	Na ₂ SO ₄
Fe ³⁺	0.01	2.5	0.41	0.29	0.19	0.88
	0.05		0.47	0.36	0.32	0.64
	0.10		0.58	0.48	0.44	0.52
	0.50		0.80	0.76	0.64	0.43
	1.00		0.84	0.82	0.72	0.38
Cu ²⁺	0.01	4.5	0.1	0.08	0.06	0.64
	0.05		0.2	0.13	0.09	0.58
	0.10		0.34	0.25	0.14	0.48
	0.50		0.46	0.32	0.28	0.32
	1.00		0.56	0.46	0.42	0.18
Cd ²⁺	0.01	5.0	0.33	0.11	0.12	1.14
	0.05		0.45	0.23	0.24	1.11
	0.10		0.67	0.34	0.34	0.78
	0.50		0.93	0.78	0.56	0.68
	1.00		0.98	1.22	0.65	0.34
Zn ²⁺	0.01	5.0	0.22	0.09	0.09	0.70
	0.05		0.37	0.14	0.14	0.62
	0.10		0.44	0.24	0.26	0.47
	0.50		0.58	0.56	0.46	0.38
	1.00		0.77	0.72	0.58	0.19
Ni ²⁺	0.01	4.5	0.12	0.01	0.09	0.53
	0.05		0.20	0.04	0.11	0.45
	0.10		0.28	0.7	0.17	0.32
	0.50		0.34	0.25	0.20	0.26
	1.00		0.44	0.29	0.26	0.11
Pb ²⁺	0.01	6.0	0.52	0.23	0.23	1.62
	0.05		0.58	0.46	0.42	1.22
	0.10		1.45	0.76	0.78	0.89
	0.50		2.66	1.67	1.66	0.61
	1.00		2.88	2.17	1.92	0.42

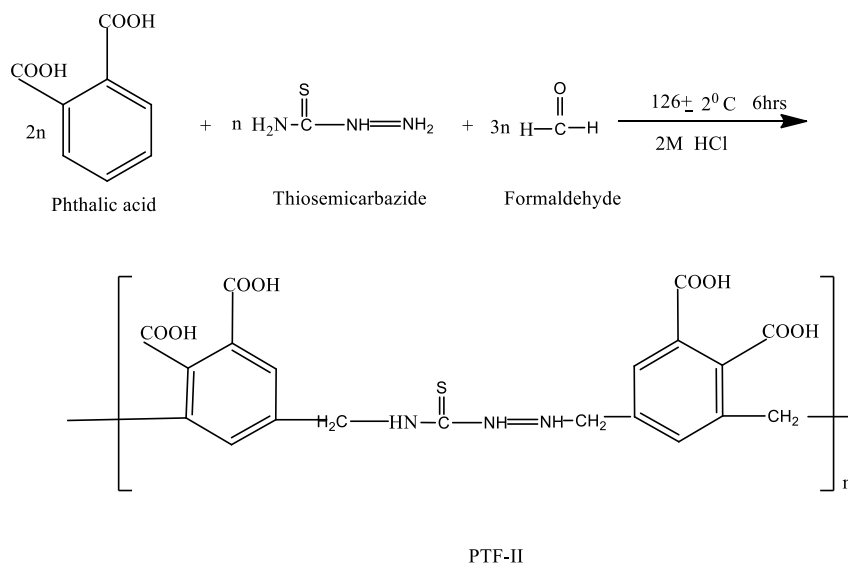


Fig.1. Synthesis of PTF-II Copolymer Resin

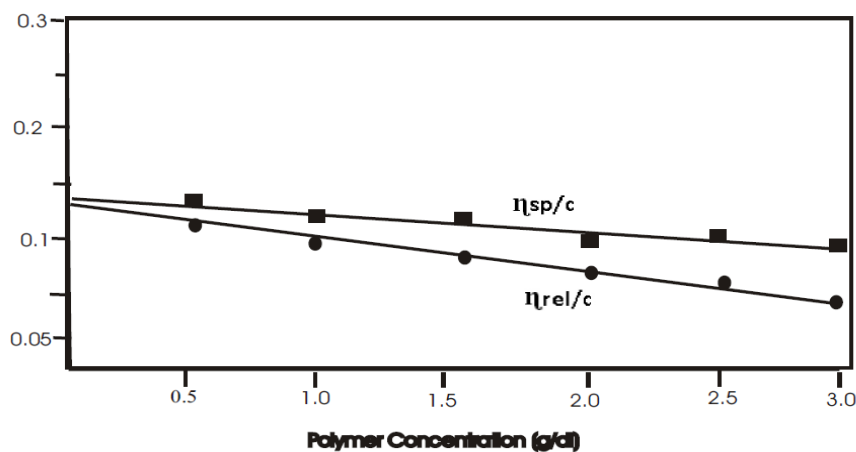


Fig.2: Viscometric plots of PTF-II Terpolymer

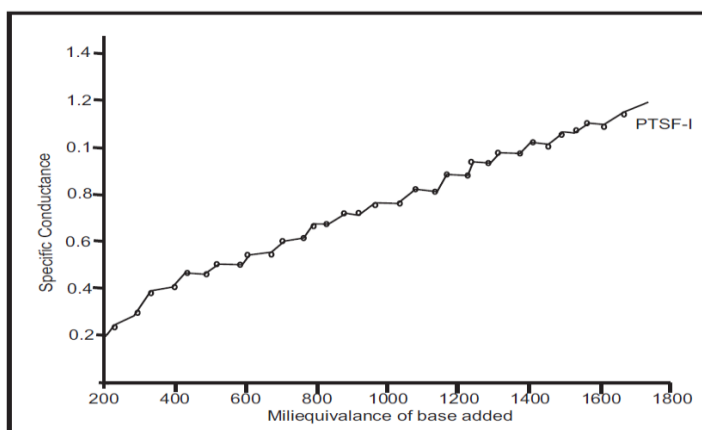


Fig. 3. Conductometric Titration Curve

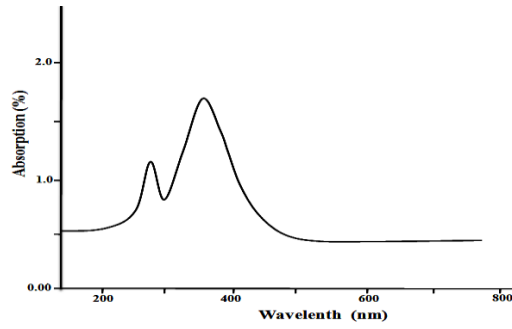


Fig. 4. Absorption spectrum of PTF-II copolymer resin

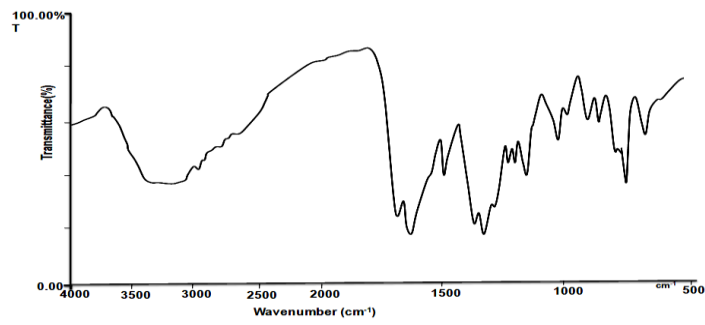


Fig. 4. Infrared spectrum of PTF-II copolymer resin

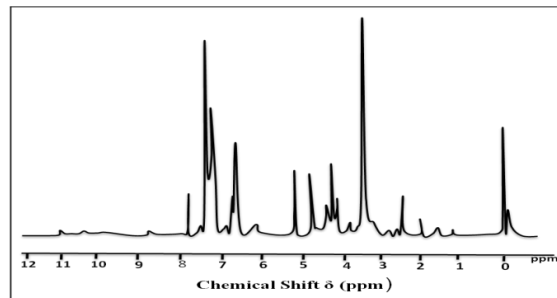


Fig. 5. Proton NMR spectrum of PTF-II copolymer resin

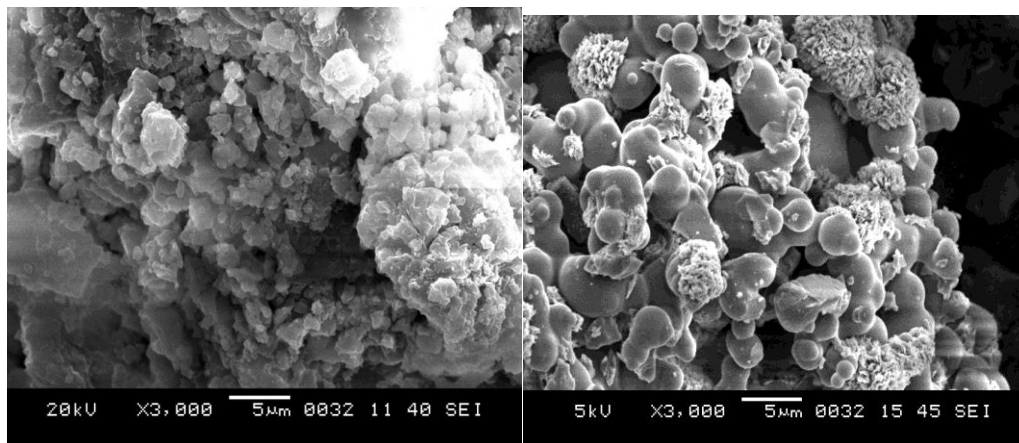


Fig 6. SEM micrograph of PTF-II copolymer resin