Synthesis and Application of Conducting polymers for the removal of heavy metals from Industrial effluents

R.Mahalakshmi, K.Rathina , L.Ravikumar , P.S.Syed Shabudeen

Abstract— The new poly (azomethine amide) and poly (azomethine hydrazide) were synthesised through direct polycondensation of 2(p-chlorobenzalimino)terephthalic acid with 4,4' – methylamine diamine and adipic dihydrazide in DMF using phosphorylation technique. FTIR and ^{1}H-NMR spectroscopic analysis was used to characterize the monomers and polymers The Schiff base polymers when blended with polyaniline shows good conductivity. The polymers synthesised are thermally stable which show good conducting properties and solubiltiy which have high impact on the environmental stability.

Key words: Polymers, Spectral studies, Conductivity…

I. INTRODUCTION

Simple azomethine (-CH=N- groups) compounds are well known for their liquid crystalline properties.[1,2].When the azomethine groups are incorporated into the polymer backbone they exhibit good properties such as thermal stability [3,4] conductivity[5], fibre forming ability[7] liquid crystalline behavior[8,9] and non-linear optical properties [10].The drawback of the linear , aromatic rod like polymer is the limited solubility in organic solvents. In general, rod like polymers due to strong enthalphic interaction and the minimal increase in conformational entropy associated with their dissolution or melting are basically intractable or possible only under extreme conditions .To improve the processability, structural modifications in the polymer, such as bulky lateral substituent, flexible alkyl side-chains, non-co-planar biphenyl moieties, and kinked co- monomers have been investigated.

Earlier works from this laboratory were aimed at synthesis of poly (azomethine esters)s [11] and poly(azomethine amide)s[12]. Such polymers show good corrosion control on Al in alkaline medium and good conductivity [13] when blended with different polyanilines.[14].Since the discovery of high electrical conductivity in doped polyacetylene the search for new conjugated polymers (CPs) has never stopped. They exhibit never seen before properties that could lead to many applications . Polyaniline [15] and polypyrrole were among the first one to attract interest . Among the available intrinsically conducting polymers, PANI is found to be the most promising because of its low cost, ease of synthesis, and tunable properties. The doping process was found to be most important factor in the achievement of a high level of conductivity for PANI. Moreover, PANI synthesized in different acidic solutions, such as 2-chloroethylphosporic acid, 5-sulphosalicilic acid, and benzene sulphonic acid , also improves the processability and conductivity [16]. A better method for successful utilization of PANI is through blending it with either commercially available polymers [17] or with new polymers [18]. It can also be used as a conducting filler in suitable conjucate polymers such as polyazomethines. There is a wider scope for the practical application of such composites [19,20].

The objective of the present work was to synthesize new polyamides and hydrazides having pendent benzylidine groups and to study their conductivity and processability by blending with minimum percentage of PANI synthesized in dil. HCl. This study is of particular interest due to the fact that the blend composition is solution-processable in common organic solvents and have high influence on industrial effluents for removing heavy metals.

II. EXPERIMENTAL

A. Materials, Solvents

N.N-Dimethylformamide (LR, BDH) was kept for 24 hours and distilled under reduced pressure. N.N-Dimethylacetamide (LR, BDH) was first kept over KOH for 24 hours and then over P_2O_5 for 24 hours and finally distilled under reduced pressure. Pyridine (LR, BDH) was kept over KOH for 24 hours and distilled. All other solvents used were either analytical grade or purified according to the standard procedure. 2- Amino terephthalic acid (Aldrich) was used as received. Diamino diphenyl methane (Aldrich) was recrystallised from ethanol.

B. Synthesis of Monomers , Synthesis of Dicarboxylicacids

4'-Chlorobenzalanilene-2, 5-dicarboxylic acid

Equimolar amount of 2-aminoterephthalic acid and chlorobenzaldehyde were condensed in the presence of p-toluene sulfonic acid as catalyst in DMF. After removing calculated quantities of azeotropic mixture at reduced pressure, the reaction was allowed to completion under reflux condition for 2-3 hours.The resulting solution was poured into water, to get a yellow precipitate. It was repeatedly washed with hot water, dilute sodium carbonate, water, finally with

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cold alcohol, and dried in vacuum for 6 hours. It was then recrystallized from DMF/water mixture. Adipic dihydrazide monomer was prepared according to literature reports [21].

All the polymers synthesized in this report were obtained by direct poly condensation reaction with $P(0Ph)_3$ initiated by pyridine – HCl in DMF

C. Preparation of Polymers/ Polyaniline blends

Polyaniline (PANI) was synthesized by oxidation polymerization of distilled aniline with $(NH_4)_2S_2O_8$..Polyaniline was treated with 0.1M HCl solution for 2h filtered and dried in vacuum at 40^0c for 6 h to get PANI/HCl powder. The dried powder stored is in a desiccator for more than 6 months were used for the preparation of various blends.

Polymers/ Polyaniline in the required weight ratio percentage were weighed and the powder was grounded in crucible for homogeneous mixing .The powder was put in a hydraulic press of load 5 tons, for making the pellets. To exclude moisture, the pellets were dried in an oven at 40^0c under vacuum for 6 h. The pellet sizes are 10.06mm in diameter and thickness of 1.52mm

D. Characterization

Viscosity measurements of the polymers were carried out in an Ubbelohde suspended level viscometer at 30 ± 0.1^0C in DMF. IR spectra of monomers and polymers were recorded on a FTIR spectrophotometer using KBr pellet.^{1}H-NMR of one the monomer were recorded on a varian XL-300 spectrometer in DMSO-d_6. TGA measurements were recorded on a Perkin-Elmer analyzer, with a heating rate of 10^0C/min..Solubility of the polymers were tested with 2-3ml of solvent at room temperature.

E. Results and Discussion: Sythnesis of Monomers:

4'-Chlorobenzalaniline-2,5 – dicarboxylic acid was synthesized based through the procedure established in our laboratory. IR spectrum of the 4-amino terephthalic acid and monomer p-chlorobenzamiloterephthalic acid are shown in Fig1.The disappearance of characteristic stretching frequency of primary amino groups of 2-aminoterephthalic acid and the appearance of aromatic – CH and imine –CH stretching frequencies at 2876 cm^{-1} and 2945 cm^{-1} respectively supports the formation of azomethine link in the monomer [22]. The -CH=N- stretching frequency appears at 1611 cm^{-1} which is within the reported range of 1610 to 1640 cm^{-1} [23] . The carbonyl stretching frequency of the acid groups appears at 1693 cm^{-1}.

The ^{1}H-NMR spectrum of 4'-Chlorobenzalanilene-2,5 – dicarboxylic acid is shown in Fig 2. The δ values are assigned in the figure itself. Monomer adipic dihydrazide was synthesized according to the literature reports [24]. IR spectrum of the monomer adipic dibydrazide is shown in Fig3. Characteristic asymmetric and symmetric stretching frequency of primary amino group appear at 3315 cm^{-1} and 3290 cm^{-1} respectively. The C=0 stretching frequency appears at

1631cm^{-1}. The rocking deformation of -$(CH_2)_4$ appears 744cm^{-1}. The region 1500-1400 cm^{-1} will be due to coupled vibrations of –NH bending and aromatic ring vibrations. However, a band at 1490 cm^{-1} may be assigned to predominantly –NH bending [25]
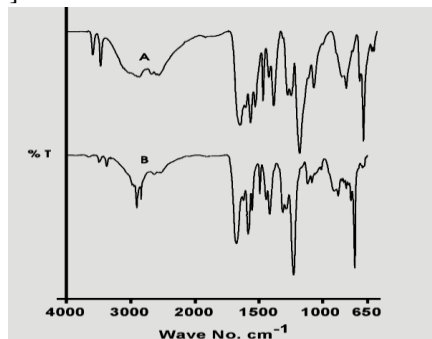

Fig-1. IR-Spectra of A : 4 - aminoterephthalic acid
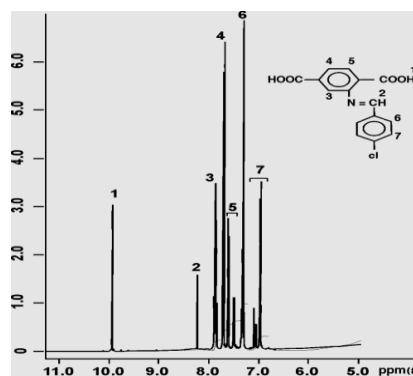B : 2 - (p-chlorobenzalimino) terephthalic acid

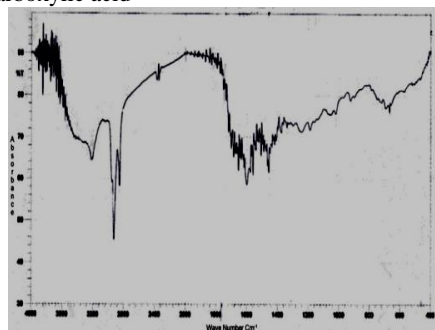Fig 2 'H-NMR spectrum of 4'-Chlorobenzalanilene-2,5 – dicarboxylic acid
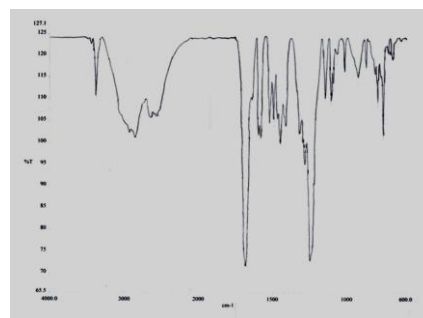

Fig 3 - IR spectrum of the monomer adipic dibydrazide

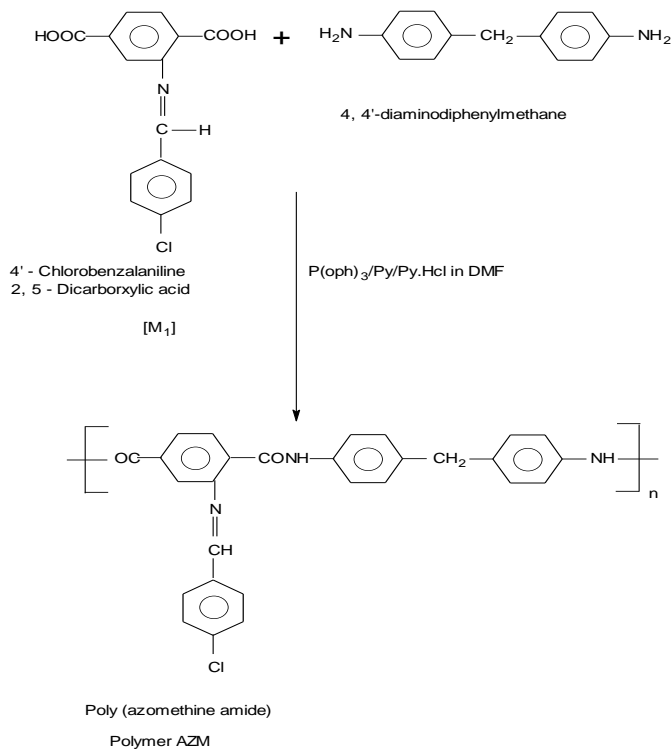Fig 4: IR spectrum of polyazomethine amide AZM

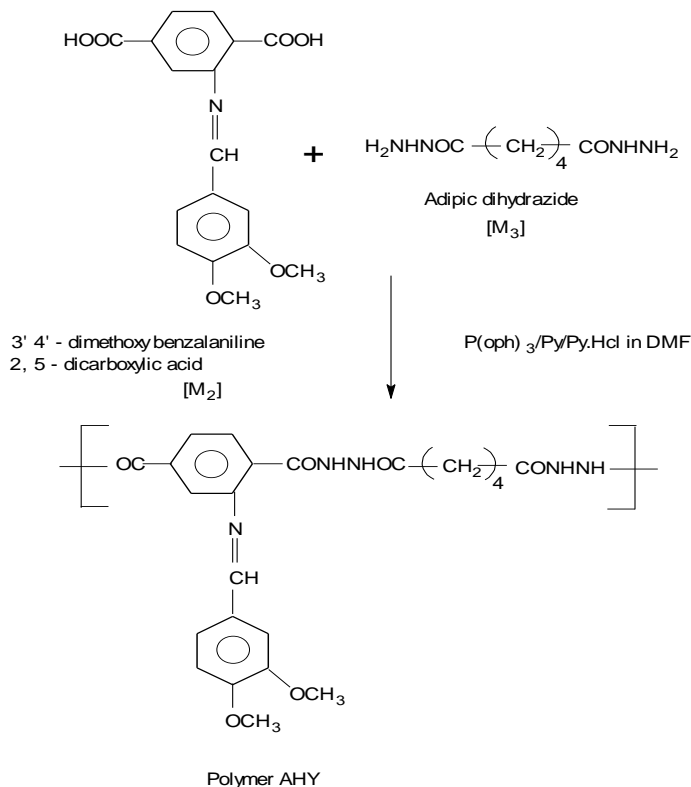
Synthesis of Polymer

Polymer synthesis is outlined in scheme 1 and 2.

Scheme-1

Scheme -II

Polymers are light yellow coloured due to the presence of - N=CH- groups and the inherent viscosities of the polymers AZM and AHY are 0.35 and 0.46 respectively. The viscosity values are comparable to those that of poly (azomethine ester)s of similar type synthesized from this laboratory [26]. The viscosity values suggests that the synthetic approach for the polyamides through phosphorylation method adopted in this work is a highly successful method..

The IR spectra of polyazomethine amide(AZM) is shown in fig 4. The aromatic ring CH and imines -CH stretching frequencies appeared at 2854 and 2957 cm-1 respectively.Formation of polymer is strongly supported by the absorptions due to –CONH- link. In the polymer the –NH stretching frequency shows a strong absorption at $3382 cm^{-1}$. The -CH=N- stretching frequency observed in the monomer at $1611 cm^{-1}$ is retained in the polyamides at $1592 cm^{-1}$. The carbonyl stretching frequency shows absorptions in the range 1660-1680 cm^{-1}. In the present case the C=O stretching frequencies of the polyamides shows strong absorption bands at $1682 cm^{-1}$. The ^{1}HNMR spectra of AZM is shown in fig 5
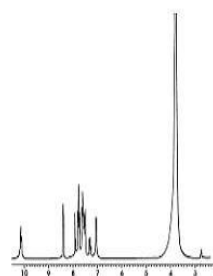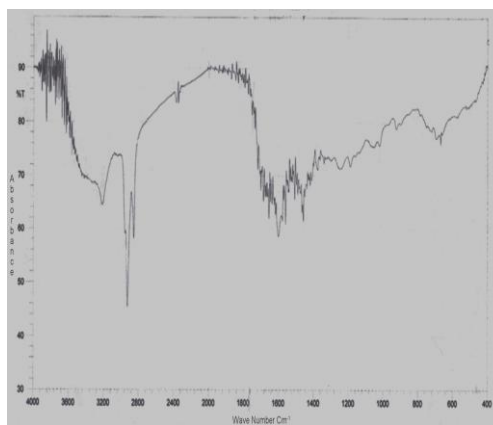

Fig 5 HNMR spectra of polyazomethine amid

Fig 6   IR spectrum of Polyazomethine

The amide protons appeared at   10.1 ppm.The peak observed at 8.2 ppm is due to the CH=N- protons. The aromatic protons appears as wider signal in the range 7.7-6.8 ppm.The chemical shifts are in good agreement with the proposed polyazomethine amide structure..The IR spectrum of polyhydrazide AHY is shown in fig 6. Assymmetric and symmetric stretching frequency of the NH_2 groups in the

monomer is assigned to bands at 3315 cm^{-1} and 3290 cm^{-1} respectively. In the polymer the NH_2 absorption, as expected, is absent. Formation of -CONH- link is established by the disappearance of -NH_2 absorption and the appearance of -NH stretching frequency of the amide link at 3215cm^{-1}. The carbonyl stretching frequency appeared at 1631 cm^{-1} for the monomer is retained in the polymer at 1635cm^{-1} . The -CH = N- stretching frequency in the polymer appears at 1602cm^{-1} which is absent in the dihydrazide monomer.The aromatic ring -CH and imine -CH stretching frequencies in the polyhydrazide appear at 2852 cm^{-1} and 2923cm^{-1} respectively.

III. THERMAL STUDIES:

The thermal behaviour of the two polymers synthesized were observed with TGA in nitrogen atmosphere. The TGA curves of the polyazomethine amide and poly azomethine hydrazide is given in Fig 7 and 8.

The thermal analysis data of the polymers examined by TGA are summarized in Table 1. Making due compensation for the initial weight loss due to loss of adsorbed solvent and moisture, the initial decomposition temperature (T_o), temperature at which 10% weight loss(T_{10}) at 20% weight loss (T_{20}) along with clear yield at 700°C (%) are compared in Table 1.

Table -1

Thermal analysis data

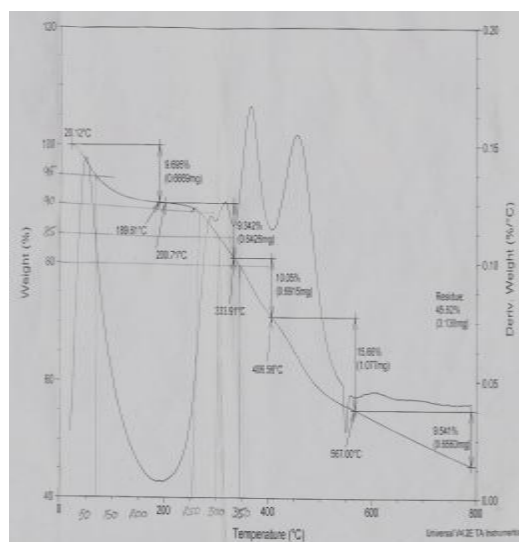| Polymer	$T_0(^0c)$	$T_{10} (^0c)$	$T_{20} (^0c)$	Char yield at 700^{0}C(%)
AZM	245	258	346	45.6%
AHY	160	257	280	34.4%

Fig 7 -TGA curve of the polyazomethine amide

The poly (azomethine amide) AZM under goes major degradation in two steps in the temperature 300-560^{0}c respectively. However, the poly (azomethine hydrazide)AHY undergoes major degradation in a single step in the

temperature range 250-350^{0}C, with a char yield of 34% at 700^{0}C. The higher thermal stability of poly (azomethine amide) are attributed to the wholly aromatic nature of the polymers. The lower thermal stability of the poly(azomethine hydrazide) is due to the aliphatic flexible spacer (CH)$_4$ present in the polymer back-bone. Thermal analysis of the polymers suggests that then presence of benzylidine moiety as a pendent group in the polymer has not decreased the thermal stability.
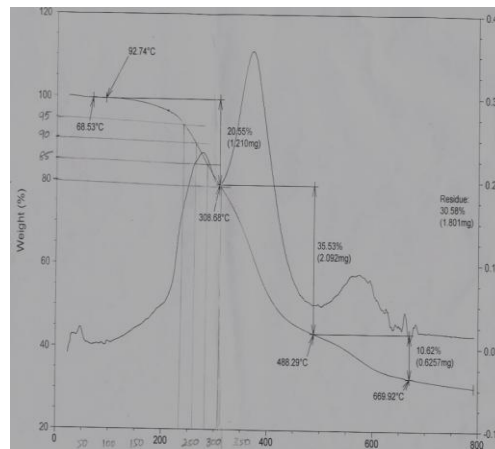

Fig 8 -TGA curve of the polyazomethine hydrazide

IV. SOLUBILITY

Solubility of the synthesized Polymers are given in Table 2.

Table - 2

Polymer Solubility

Solvent	AZM	AHY
DMF	++	++
NMP	++	++
DMSO	++	++
Pyridine	+-	+-
DMAC	+-	+-

++ Soluble   +- Partially soluble   -- Insoluble

It is evident from Table 2 that all two polymers are soluble in solvents like DMF, DMAC, DMSO and NMP apart from conc.H_2SO_4. They are partially soluble in pyridine and insoluble in benzene and acetone.The improved solubility of poly(azomethineamide)s and poly(azomethine hydrazide) are clearly due to the pendent benzylidine rings.

V.CONDUCTIVITY:

Conductivity measurements of Polymer blends

Table - 3

Polymer Blend	Conductivity (Scm^{-1})
PANI/HCl	2.1

AZM/20% PANI /HCl	1.6×10^{-3}
AHY/20% PANI /HCl	3.5×10^{-3}

Conductivity studies of PANI/HCl and the Polymer blends are shown in Table 3. The Polymeric blends AZM/20% PANI /HCl and AHY/20% PANI /HCl showed conductance in the range 1.6 to 3.5×10^{-3} suggesting that AHY is a better host than AZM. Further studies on the conductance of Polymers are under progress.

VI. CONCLUSION

In this study a new polymer adsorbent was synthesized and the adsorption properties were investigated. The Polyamide and Polyhydrazide with pendent chlorobenzalaniline moieties were synthesized. The Polymers exhibited thermal stability along with better solubility. When blended with PANI/HCl they showed good conductivity in the range of $1.6- 3.5 \times 10^{-3}$ Scm^{-1} which show high influence on industrial effluents for removing heavy metals. The characterization of polymer studies also clearly established that the newly developed polymer is rapid in sensing the metal ions which is vital for any analytical procedure.

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