

Synthesis and Characterization of Poly Schiff Bases Derived from 5a,10b-Dihydrobenzofuro [2,3-b] benzofuran-2,9-dicarbaldehyde with Various Diamines

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Received 30 December 2001; accepted 15 September 2002

ABSTRACT

Three new poly Schiff bases were synthesized by polycondensation of diethylenetriamine, 1,2-diaminopropane and *o*-diaminobenzene with 5a,10b-dihydrobenzofuro [2,3-b] benzofuran-2,9- dicarbaldehyde II. The polymers have been characterized by their FTIR and ¹H NMR spectra. The relationship of thermal stability of these polymers to their chemical structure was studied by thermogravimetric analysis (TGA) and differential Scanning calorimetry (DSC). Their average molecular weight was determined by GPC. These Schiff base polymers are soluble in common organic solvents. The poly Schiff base III copper complex was prepared and characterized by FTIR and UV/vis. The polymer chelate was insoluble in common organic solvents.

Iranian Polymer Journal, 12 (1), 2003, 43-50

Key Words:

polycondensation;
poly Schiff base;
polymer chelate;
diamine.

INTRODUCTION

Polymeric Schiff bases have been the subject of numerous studies, after the pioneering investigations of D'Alelio's et al. at the end of the 1960s [1,2]. Poly Schiff bases were synthesized by polycondensation of dialdehydes or diketones with

aliphatic or aromatic diamine to give high molecular weight polymers. However, their rigidity causes poor solubility in organic solvents limited their practical applications in various fields [3]. One way to improve the solubility is to add flexible side

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chains onto polyazomethines [4,5]. Schiff base polymers usually show base properties because of the C=N linkage in backbone. Interest has been focused on poly Schiff bases because of their thermal stability, potential semiconducting or conducting properties when aromatic units are introduced in the main chain, and non-linear optical properties [6-8].

Coordination polymers derived from polymeric Schiff bases have been extensively studied [9,10]. It is known that reaction of metal ions with organic ligands produces coordination systems having enhanced thermal stability and often improved chemical resistance [11-14].

Entezami et al. reported that the polymer derived from 5a,10b-dihydrobenzofuro [2,3-b] benzofuran-2,9-dicarbaldhyde II with bis (cyanoacetate) monomer by Knoevnegel polycondensation in anhydrous THF has been having third-order non-linear optical. In this work, dihydrofuran derivatives as donor and bis (cyanoacetate) as acceptor parts were selected [15].

The aim of this work was to prepare poly Schiff base by polycondensation of 5a,10b-dihydrobenzofuro[2,3b]benzofuran-2,9-dicarbaldhyde II with numerous diamine and study their properties metal chelating. The relationship of thermal stability of these polymers to their chemical structure was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as well as the average molecular weight of these polymers were determined by GPC.

EXPERIMENTAL

Materials

All the reagents as diethylenetriamine, o-diaminobenzene and solvents used in this work were purified by conventional methods [16]. For the preparation of poly-chelate, metal acetate used was of Riedel-De Haen Ag Seelze-Hannover grade.

Nitro phenol (Merck) is converted readily to aminophenol in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in alcohol, yield 97% mp 179°C [17].

Characterization

The FTIR spectra of the compounds were recorded from KBr pellets by Shimadzu 4300 FTIR spectrophotometer over the range of 4000-400 cm^{-1} .

Spectrophotometric studies in acetic acid glacial were carried out on Shimadzu 2100 spectrophotometer.

The melting points are uncorrected and were deter-

mined on Electrothermal 9100. Thermal analysis TGA and DSC were carried out on STA 625 analyzer and gel permeation chromatography was carried out on a Maxima 820 by using DMF as an eluent after calibration with standard polystyrene samples. The ^1H NMR spectra were recorded in DMSO- d_6 , CDCl_3 solution on 500 MHz, 90 MHz instrument and chemical shifts were reported in ppm units with TMS as an internal standard.

Synthesis

5a,10b-Dihydrobenzofuro[2,3-b]benzofuran-2,9-dicarbaldhyde II was prepared in two steps from p-cresol and glyoxal:

5a,10b-Dihydro-2,9-dimethylbenzofuro[2,3-b]benzofuran I was prepared from p-cresol and glyoxal [18].

Synthesis of 5a,10b-Dihydrobenzofuro[2,3b] benzofuran-2,9-dicarbaldhyde II

To the solution of compound I (1 g, 4.2 mmol) in acetonitrile (60 mL) was added ammonium persulphate (5.7 g, 25 mmol), copper sulphate (0.62 g, 2.5 mmol) in water (60 mL). Pyridine (2 mL) was added to mixture and stirred at 65-70°C for 4 h. Then, the reaction mixture was cooled down, followed by adjusting pH 9 with 5% aqueous sodium hydroxide. The organic layer was extracted three times with ethylacetate, washed with water for three times and dried with anhydrous CaCl_2 . The solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography with an eluent of ethylacetate-petroleum ether (3:1) to yield II. The silica-gel TLC analysis using a mixture of ethylacetate-petroleum ether (3:1) as an eluent revealed that the compound II completely purified. A white powder (60%, mp 217-219°C) was obtained [15].

^1H NMR (CDCl_3): δ 9.94 (s, 2H, CHO), 6.95-8.07 (m, 7H, aromatic proton and 5a tetrahydrofuran) and 5.15 (d, 1H,10b). FTIR, $\nu(\text{cm}^{-1})$: 3060, 2900, 2780, 1695, 1618, 1449, 1256 and 996.

Preparation of Poly Schiff Bases

Synthesis of Poly Schiff Base III from Dialdehyde II and Diethylenetriamine

Poly Schiff base III was prepared from dialdehyde II and diethylenetriamine as described below:

To a mixture of compound II (0.1g, 0.375 mmol) and lithium chloride (0.159 g, 3.75 mmol) in THF

(7 mL) was added solution of diethylenetriamine (0.038 g, 0.375 mmol) in THF (1 mL). It immediately gave a cream precipitate that was stirred for 3 h to complete reaction. The resulting precipitate was filtered and washed with methanol and acetone and then it was dried in vacuum. The product was then purified by dissolution in DMSO and reprecipitation by addition of methanol.

$^1\text{H NMR}$ (DMSO- d_6): δ 8.20(d, 2H, CH=N), 6.78-8.90 (m, 7H, aromatic protons and 5a tetrahydrofuran) and 5.20 (d, 1H, 10b), 3.40 (6H, CH_2 and end NH_2), 2.81 (s, 1H, NH), 2.50 (8H, CH_2 and DMSO). FTIR, $\nu(\text{cm}^{-1})$: 3418, 3025, 2928-2841, 1645, 1610, 1487, 1443, 1252. UV/vis, (in acid acetic), $\lambda(\text{max})$: 265 nm.

Synthesis of Poly Schiff Base IV from Dialdehyde II and 1,2-Diaminopropane

Poly Schiff base IV was prepared from dialdehyde II with 1,2-diaminopropane in the same manner described above:

To a solution of dialdehyde II (0.1 g, 0.375 mmol) and lithium chloride (0.159 g, 3.75 mmol) in the THF (7 mL) was added solution of 1,2-diaminopropane (0.028 g, 0.375 mmol) in THF (1 mL). It immediately gave a white solid. The resulting precipitate was filtered and washed with methanol and acetone several times and dried in vacuum. The product was then purified by dissolution in DMSO and reprecipitation by addition of methanol.

$^1\text{H NMR}$ (DMSO, d_6): δ 8.15 (2H, d, CH=N), 6.85-8.0 (m, 7H, aromatic protons and 5a tetrahydrofuran), 5.20 (d, 1H, 10b), 4.0 (d, 2H, CH_2), 3.45 (m, 1H, CH), 3.33 (s, end NH_2), 2.50 (s, DMSO), 1.30 (d, 3H, CH_3). FTIR, $\nu(\text{cm}^{-1})$: 3375, 3039, 2970, 2845, 1643, 1610, 1487, 1250.

Synthesis of Poly Schiff Base V from Dialdehyde II and *o*-Diaminobenzene

To a solution of compound II (0.1 g, 0.375 mmol) and lithium chloride (0.159 g, 3.75 mmol) in the THF (7 mL) was added solution of *o*-diaminobenzene (0.04 g, 0.375 mmol) in THF (1 mL). The mixture was heated to reflux for 18 h and light brown solid was obtained. The resulting precipitate was filtered and washed with methanol and acetone several times and dried in vacuum. The product was then purified by dissolution in DMSO and reprecipitation by addition of methanol.

$^1\text{H NMR}$ (DMSO): δ 8.60 (s, 2H, CH=N), 8.03 (d, 1H, 5a), 7.60 (m, 4H, aromatic protons), 7.20 (m, 6H, aromatic protons), 5.48 (d, 1H, 10b), 2.50 (s, 10H, DMSO, end NH_2). FTIR, $\nu(\text{cm}^{-1})$: 3416, 3061, 1622, 1481, 1443, 1234.

Preparation of Copper Complex

For preparation of the complex, the hot solution of the poly Schiff base III was mixed with a molar amount of salt.

To the hot solution of poly Schiff base III (0.1 g) in DMF (10 mL) was added solution of copper (II) acetate monohydrate (0.0625 g) in DMF (2 mL). The colour of the mixture gradually changed to dark green that was heated to reflux for 6 h. The precipitate was filtered and washed with absolute ethyl alcohol and ethyl ether and then it was dried in vacuum. A green powder (23%) was obtained and decomposed above 340°C.

FTIR, $\nu(\text{cm}^{-1})$: 3408, 2837, 1595, 1426. UV/vis, (in acid acetic) $\lambda(\text{max})$: 296 nm.

RESULTS AND DISCUSSION

The dialdehyde II was prepared in two steps from *p*-cresol and glyoxal. The synthetic routes is illustrated in Scheme I.

The dialdehyde structure was investigated by $^1\text{H NMR}$ and FTIR spectroscopy. The FTIR spectrum showed a strong absorption band at 1695 cm^{-1} assigned to the carbonyl stretching vibration. The weak band at 2780 cm^{-1} is assigned to C-H aldehyde stretching vibration. The bands at 1618 cm^{-1} and 1449 cm^{-1} were due to

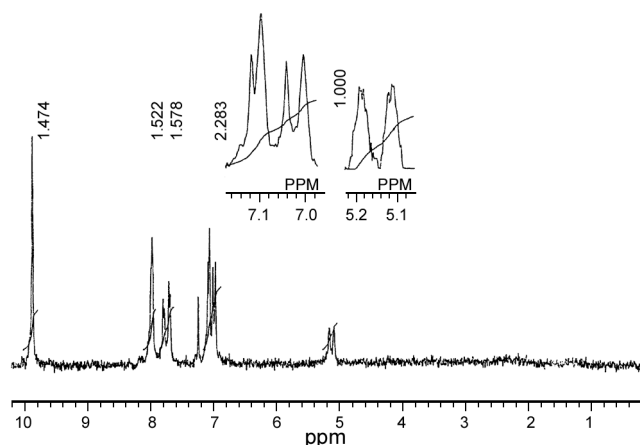
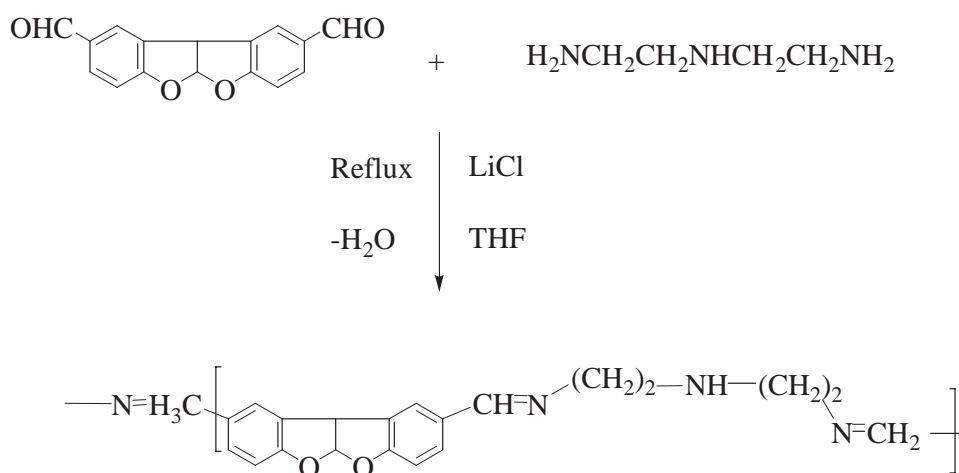
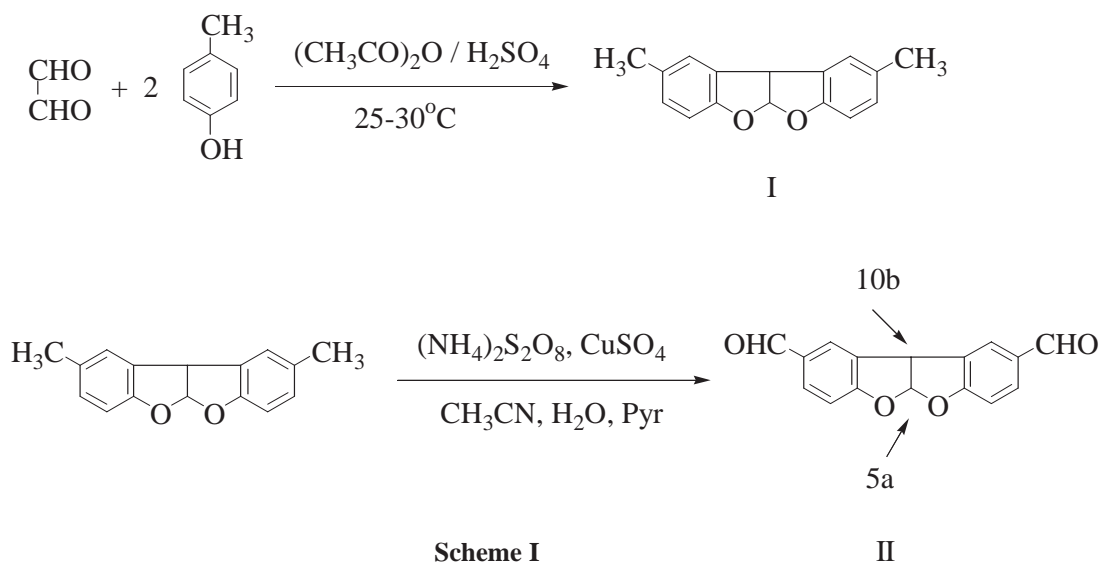


Figure 1. $^1\text{H NMR}$ Spectrum of compound II in CDCl_3 .



benzoid rings. The absorption band at 1256 cm^{-1} is assigned to C-O phenolic stretching vibration.

Figure 1 shows the ^1H NMR spectrum of compound II. The ^1H NMR Spectrum displayed a signal at 9.94 ppm that is attributed to the aldehyde proton. The signals due to the aromatic protons appeared at 6.95-8.0 ppm. The doublet at 5.15 ppm is assigned to the furan (10b) proton. The doublet at 8.07 ppm is assigned to the furan (5a) proton.

To prepare a poly Schiff base, we applied an equimolar ratio of diamine to dialdehyde and paid careful attention to absolutely dring the solvent. The poly

Schiff base III was synthesized by polycondensation of the dialdehyde II with diethylenetriamine in anhydrous THF and lithium chloride, which was used as a water absorbing reagent [3]. The poly Schiff base III is outlined in detail in Scheme II.

The structure of the polymer shown is consistent with ^1H NMR and FTIR spectroscopic data.

As polymerization proceeded, the aldehyde proton peak at 9.94 ppm disappeared and a new peak for imino proton at 8.20 ppm appeared in ^1H NMR. The signals due to aromatic protons and 5a proton appeared at 6.78-8.0 ppm. The peaks at 3.40 ppm and 2.50 ppm, respec-

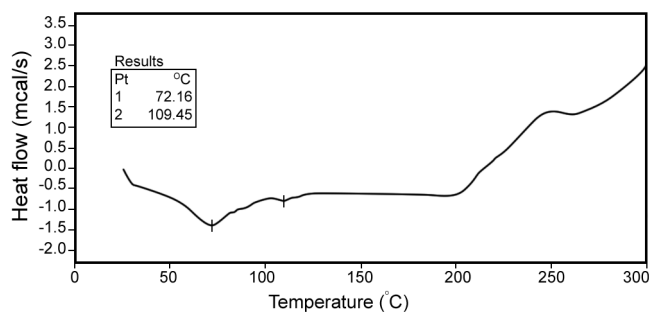


Figure 2. The DSC curve of poly Schiff base III. 10°C/min in N₂.

tively correspond to the methylene protons closer to the imino group. The singlet at 2.81 ppm corresponds to the NH group. The broad resonance at 3.40 ppm that has interfered with peak CH₂ could be due to terminal NH₂ groups. The peak of DMSO is appeared at 2.50 ppm that has interfered with CH₂.

The peak FTIR spectrum of poly Schiff base III gives peaks at 3418 cm⁻¹ corresponding to NH₂ end group and NH, 3025 cm⁻¹ due to CH aromatic, 2928-2841 cm⁻¹ due to CH aliphatic, 1645 cm⁻¹ corresponding to C=N, the bands at 1645-1610 cm⁻¹ and 1487-1443 cm⁻¹ owing to benzoid rings, and 1256 cm⁻¹ corresponding C-O phenolic.

The poly Schiff base IV was prepared by polycondensation of dialdehyde II and 1,2-diaminopropane according to the following reaction equation.



The polymer structure was investigated by ¹H NMR and FTIR spectroscopy. The FTIR spectrum of poly Schiff base IV gives peaks at 1643 cm⁻¹ corresponding to C=N, 3039 cm⁻¹ due to CH aromatic, 2845-2970 cm⁻¹ due to CH aliphatic, 3375 cm⁻¹ due to NH₂ of end amine, 1250 cm⁻¹ corresponding to C-O. The ¹H NMR spectrum displayed a signal at 8.15 ppm that is attributed to the imine proton. The signals due to aromatic

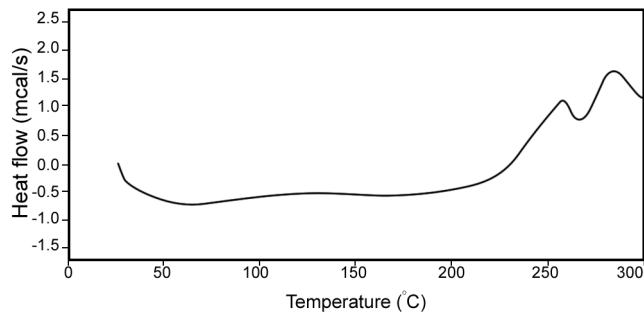


Figure 3. The DSC curve of poly Schiff base IV. 10°C/min in N₂.

protons and 5a proton were appeared at 6.85-8.0 ppm. The doublet at 5.20 ppm is assigned to the furan (10b) proton. The peak DMSO appeared at 2.50 ppm. The peak of NH₂ end was appeared at 3.33 ppm. Gel permeation chromatography (GPC) with polystyrene as a standard showed weight average molecular weight (MW) to be about 3179 with a polydispersity of 1.09.

The poly Schiff base V was prepared by polycondensation of dialdehyde II and *o*-diaminobenzene. The reaction pathway is shown below:



The polymer structure was investigated by ¹H NMR and FTIR spectroscopy. The FTIR spectrum of poly Schiff base V gives peaks at 1622 cm⁻¹ corresponding to C=N, 3061 cm⁻¹ due to CH aromatic, 3416 cm⁻¹ due to NH of amine, and 1234 cm⁻¹ corresponding to C-O. The ¹H NMR spectrum displayed a signal at 8.60 ppm that is attributed to the imine proton. The signals due to aromatic protons appeared at 7.18-7.69 ppm. The doublet at 5.48 ppm is assigned to the furan (10b) proton. The doublet at 8.50 ppm is assigned to the furan (5a) proton. A singlet at 2.50 ppm could be due to terminal NH₂ group and DMSO. The gel permeation chromatography (GPC) with polystyrene as a standard showed weight average molecular weight

Table 1.

Polymer	Yield(%)	Decomposition temperature (°C)	\bar{M}_w	\bar{M}_n	Polydispersity	Solubility in hot DMF or DMSO
III	88.2	293	-	-	-	+
IV	100	286	3179	2911	1.09	+
V	63.65	255	3421	3285	1.04	+

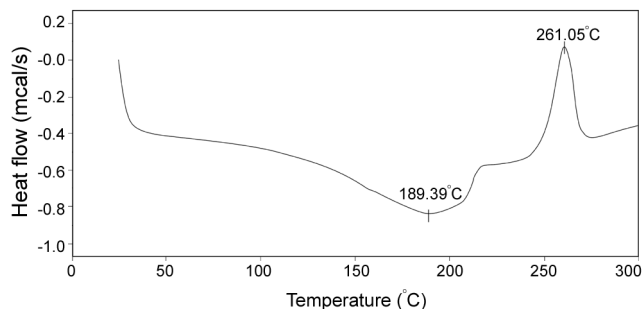


Figure 4. The DSC curve of poly Schiff base V. 10°C/min in N_2 .

(MW) to be about 3421 with a polydispersity of 1.04.

The FTIR spectra of all the polymers exhibited a strong absorption at $1645\text{--}1622\text{ cm}^{-1}$, characteristic of imine band, while absorption due to aldehyde carbonyl ($C=O$) functional group of the monomer disappeared, also at the 1H NMR spectra, The aldehyde proton peak at 9.94 ppm was disappeared [19,20].

The results of polycondensation are summarized in Table 1.

TGA and DSC were carried out to evaluate the thermal stability of the polymers prepared. The DSC curve of polymer III gave two exothermic peaks at 72.16°C and 109.45°C and an endothermic peak at 293°C . The DSC curve of polymer IV gave two endothermic peaks within $250\text{--}300^\circ\text{C}$. The DSC of polymer V gave an exothermic peak at 189.39°C and an endothermic peak at 261.05°C . The endothermic peaks probably attributed to phase transition and the exothermic peaks attributed to decomposition compound. They are shown in Figures 2-4.

The TGA curves of polymers show the loss in weight in two or four stages. The initial loss 1-6% in the temperature range $50\text{--}100^\circ\text{C}$ may be due to absorbed water or solvent. The other stages of weight loss are dependent on polymer structure and may be

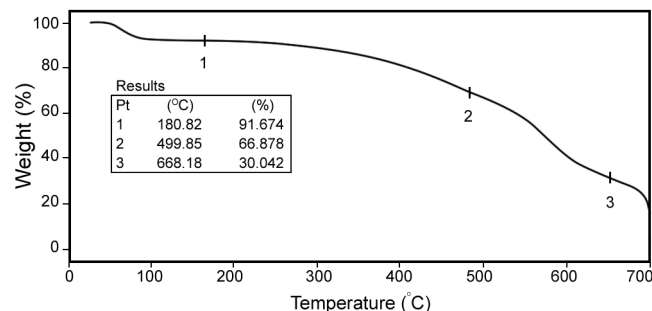


Figure 5. The TGA curve of poly Schiff base III. 20°C/min in air.

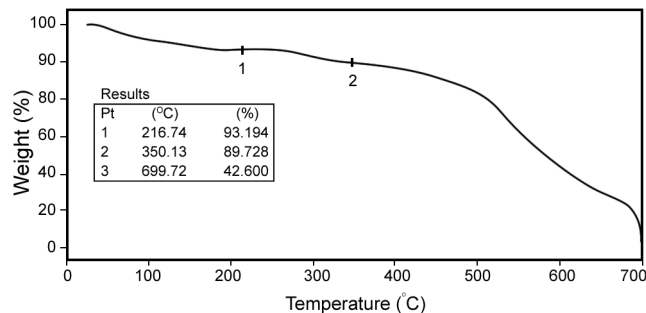


Figure 6. The curve TGA of poly Schiff base IV. 20°C/min in air.

attributed to decomposition. The total weight loss at 700°C for all the poly Schiff bases was found to be in the range 51.58-69.96%. They are shown in Figures 5-7. Thermal stability studies of the poly Schiff bases up to decomposition point indicate that they are thermally stable. Aromatic backbone units are much more stable than aliphatic one, when the temperature was raised to 700°C , the poly Schiff base V still kept more than 48% of its original weight. It is known that the higher thermal stabilities of the poly Schiff base are due to numerous factors, such as molecular weight, steric effects and resonance energy along the backbone chain.

For preparation of the complex, the hot solution of the poly Schiff base III was mixed with a molar amount of metal salt dissolved in DMF. The color of the mixture gradually changed, which may be due to formation of a complex. The complex is insoluble in common organic solvents except glacial acetic acid.

On comparison of FTIR spectra of ligand and its polychelate, it is inferred that they are virtually identical with each other. However, they show important differences. The strong band of $C=N$ in ligand at 1645 cm^{-1} show negative shift in polychelate. The copper poly chelate is shifted to lower frequency, i.e., at 1611 cm^{-1} . The observable shift obtained in $C=N$ stretch after

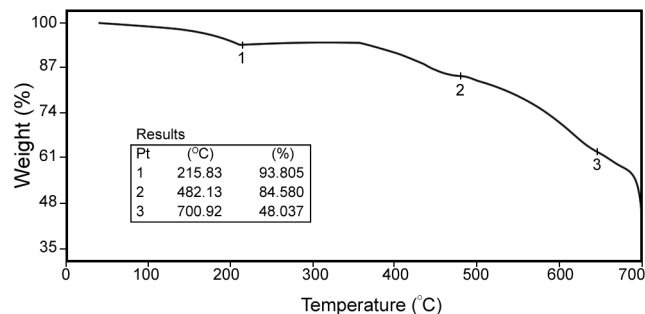


Figure 7. The TGA curve of poly Schiff base V. 20°C/min in air.

complexing confirms the formation of a coordinate bond from imine nitrogen to the metal ion. The complex contain medium intensity broad band in the region 3300-3600 cm^{-1} . The band is assigned to OH of water.

The spectrophotometric studies of poly Schiff base III and copper polychelate was carried out in glacial acetic acid. The poly Schiff base indicates bands within 265-296 nm. The bands could be assigned to $\pi-\pi^*$ transition in benzoid rings and C=N groups. The copper (II) polychelate indicate a band within 255-299 nm. Their slightly different position from the Schiff base polymer may be due to better coordination with metal ion. The copper polychelate indicates a band at 699 nm. The band may be due to d-d transitions.

The chelate was found to be insoluble in common organic solvents which preclude their characterization by conventional methods.

CONCLUSION

Several poly Schiff bases containing tetrahydrofuran rings have been synthesized by simple polycondensation in THF. All the polymers are soluble in hot DMF and DMSO. The spectra of all the polymers exhibited a strong absorption at 1645-1622 cm^{-1} , characteristic of azomethine band, while absorptions due to aldehyde carbonyl (C=O) functional group of the monomers disappeared. The thermal stability of the poly Schiff bases was found to depend on the chemical structures and to increase with increasing aromaticity. They have good thermal stability and major thermal decompositions observed above 250°C. All of the polymers showed excellent thermal stability with 7-10% weight loss at 300°C in air.

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