



Preparation and Characterization of Schiff Base Polythioamides Derived from [4,4'-Methylenebis(cinnamaldehyde)] by Willgerodt-Kindler Reaction

Ambreen Shah^{1*}, Mohammad Yar Khuhawar¹, and Asif Ali Shah²

(1) Dr. M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan

(2) Sindh Agriculture University, Tandojam, Sindh, Pakistan

Received 11 August 2008; accepted 1 March 2009

ABSTRACT

Five new polythioamides were prepared by polycondensation of a mixture of sulphur and various diamines with a dicarbonyl compound [4,4'-methylenebis(cinnamaldehyde)] (MBC). The used diamino compounds were ethylenediamine, 1,3-propylenediamine, meso-stilbenediamine, semicarbazide, and thiosemicarbazide. The polythioamides formed were characterized by elemental microanalysis, FTIR, UV, Vis, and ¹H NMR spectroscopies, thermal analysis and viscosity measurement. All the polythioamides indicated a characterized band within 1230-1260 cm⁻¹ due to νC=S vibrations. The synthesized polythioamides indicated better thermal stability up to 600°C. The dialdehyde (MBC) and polythioamides were soluble in number of organic solvents including tetrahydrofuran, dimethyl formamide, dimethyl acetamide, and dimethyl sulphoxide. The intrinsic viscosities of these polythioamide ranged within 0.393-0.5201 dL/g as compared to 0.174-0.249 dL/g for dialdehyde (MBC) in THF.

INTRODUCTION

Polythioamides are stable polymers, similar to polyamides in which carbonyl oxygen has been replaced by sulphur, but the melting points of polythioamides are reported to be of about 50-80°C lower than homologous aliphatic polyamides [1,2]. The hydrogen bonding is decreased due to the presence of thiocarbonyl groups in polythioamide, which may enhance solubility in solvents such as chloroform [3]. Number of polythioamides have been obtained in solution from bis(dithioesters) and diamines, including aliphatic, semiaromatic and fully aromatic [4-6]. The kinetics and mechanism

of polythioamidation in solution of mono and bis(dithioesters) with excess amines have been described [7]. Chemical transformation of polyamide to polythioamide by Lawesson's reagent, 2,4-bis(4-methoxyphenyl)1,3-diphosphetane-2,4-disulphide has also been reported as an alternative method.

The Willgerodt-Kindler reaction is a known method for the synthesis of thioamides [8] and was used for the preparation of polythioamides by coupling polycondensation of dialdehyde with diamines in the presence of sulphur [9]. Kanbara et al. [10] reported preparation of a number of poly-

Key Words:

polythioamides;
synthesis;
infrared spectroscopy;
ultraviolet-visible spectroscopy;
nuclear magnetic resonance.

(* To whom correspondence to be addressed.

E-mail: anashba_shah@yahoo.com

thioamides, by Willgerodt-Kindler type reaction involving one-pot three-component polycondensation. The compounds were obtained in moderate to good yields. Isophthalaldehyde and terephthalaldehyde gave the corresponding polythioamides in a good yield, but phthalaldehyde did not form polymers due to the steric factors. The polycondensation of hetero-aromatic dialdehyde gave polythioamides in moderate yields. Diketones, instead of dialdehydes, gave no polymeric product due to the slow dehydration of amines with diketones [10]. The reaction with cyclic secondary diamines and aliphatic primary diamine indicated good yields, but acyclic secondary diamines did not give any polymeric product [10]. Kagaya et al. [11] have used polythioamides as collectors for gold (III) and platinum (IV) from aqueous and organic solutions. Hadjidakou et al. [12] have synthesized, characterized and reported the biological study of new organotin (IV), silver (I) and antimony (III) complexes with thioamides. Lobana et al. [13] examined crystal structure of copper (II) and reported that heterocyclic compounds are also able to form copper complexes with 1,3-imidazoline-2-thio(ones) in the presence of triphenylphosphine.

The present work examines Willgerodt-Kindler type reaction for the formation of five new polythioamides by coupling polycondensation of different diamines in the presence of sulphur with a dialdehyde [4,4'-methylenebis(cinnamaldehyde)] (MBC). Polymeric products were obtained in moderate to good yields and their confirmation supported by spectroscopic, thermogravimetric and viscosities measurements.

EXPERIMENTAL

Materials

Cinnamaldehyde, ethylenediamine, 1,3-propylenediamine, semicarbazide, thiosemicarbazide (E. Merck, Germany) and 1,3,5-trioxane (Fluka, Switzerland), glacial acetic acid, sulphuric acid (98%), chloroform, *n*-hexane, sulphur, dimethyl acetamide (DMAc) and methanol obtained from (Fluka, Switzerland) were used. Pure nitrogen obtained from British Oxygen Company (BOC), Karachi, was used. Meso-stilbenediamine was prepared as reported [14] from

benzaldehyde via hydrobenzamide, acetyl-mesostilbenediamine to meso-stilbenediimine.

Apparatus

The elemental micro-analyses were carried out by a Devon elemental microanalyzer (UK). Infrared spectra were recorded on a Nicolet Avatar 330 FTIR (Thermo Nicolet Electron Corporation, USA) with attenuated total reflectance (ATR) accessory (Smart partner) within 4000-600 cm^{-1} . Spectrophotometric studies were carried out in dimethyl formamide (DMF) and tetrahydrofuran (THF) on a double beam Hitachi 220 spectrophotometer (Tokyo, Japan), with dual 1 cm silica cuvettes within 185-700 nm. Thermogravimetry (TG) and differential thermal analysis (DTA) were recorded on a Shimadzu TG 30 thermal analyzer from room temperature to 500°C with a nitrogen flow rate of 50 mL/min. Sample (10 mg) was placed in platinum crucible and it was recorded against alumina as a reference at a heating rate of 10°C/min. The nuclear magnetic resonance ^1H NMR spectra of dialdehyde and their polythioamides were recorded on a Bruker ACF300 spectrometer, using dimethylsulphoxide (DMSO) as a solvent and tetramethyl silane (TMS) as an internal reference.

The viscosity measurements of dialdehyde (MBC) and their polythioamides were noted within temperatures 283-323 K with interval of 10 K by using a Technico ASTM 445 suspended level viscometer. Each time 15 mL of solution was taken and an average flow time of at least three readings was taken. The flow time of solvent under the same condition was also noted. A Gallenkamp viscometer bath was used to control the temperature.

Preparation of 4,4'-Methylenebis(cinnamaldehyde) (MBC)

This dialdehyde was prepared as below [15]:

Into solution of 19.4 mL of cinnamaldehyde in 12.5 mL of glacial acetic acid in nitrogen atmosphere was added 1.75 g of trioxane diluted in mixture of 0.125 mL of sulphuric acid (98%) and 0.625 mL glacial acetic acid dropwise with constant stirring. Refluxing was continued for 24 h at 90-95°C and the reaction mixture cooled at room temperature and poured in 1 L ice-cold water. The contents were allowed at room temperature overnight. Solid product

was filtered and recrystallized from mixture of chloroform/n-hexane and dried at 90-100°C.

Preparation of Polythioamides

Sulphur (160 mg, 2.5 equiv as elemental sulphur for monomer) was added to 2 mmol of different diamines dissolved in 10 mL DMAc at room temperature. Stirring was continued for 10 min and during the time, the reaction mixture turned dark green. Dialdehyde (MBC) (2 mmol) dissolved in 10 mL of DMAc was added to the reaction mixture and contents were heated at 115°C for 18 h with constant stirring under nitrogen atmosphere. The reaction mixture was cooled at room temperature and poured in 100 mL methanol. The precipitates were separated by filtration, and after filtration crude product was extracted with chloroform (50 mL). The organic layer was concentrated to 5-8 mL and added into 20 mL methanol. The solid mass was filtered, washed with methanol and carbon disulphide.

(1) Poly[4,4'-methylenebis cinnamalthioyl ethylenediamine] (PMBCSen)

FTIR: 3220, 3036, 2926.03, 2870, 1501, 1397, 1280, 1205, 966, 915, 775, 603 cm^{-1} .

Analysis of $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{S}_2)_n$, calculated: C, 69.2%; H, 5.49%; N, 7.6%; S, 17.5%.

Found: C, 69.1%; H, 5.33%; N, 7.2%; S, 17.31%.

(2) Poly[4,4'-methylenebis cinnamalthioyl propylenediamine] (PMBCSPR)

FTIR: 3240, 3053, 2923, 2845, 1491, 1443, 1280, 1290, 1215, 979, 917, 822 cm^{-1} .

Analysis of $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{S}_2)_n$, calculated: C, 69.8%; H, 5.8%; N, 7.4%; S, 16.9%.

Found: C, 68.2%; H, 5.789%; N, 7.31%; S, 16.74%.

(3) Poly[4,4'-methylenebis cinnamalthioyl semicarbazone] (PMBCSSc)

FTIR: 3245, 3026, 2922, 2870, 1654, 1521, 1495, 1406, 1382, 1330, 1274, 1204, 1086, 945, 842 cm^{-1} .

Analysis of $(\text{C}_{20}\text{H}_{17}\text{N}_3\text{S}_2\text{O})_n$, calculated: C, 63.3%; H, 4.48%; N, 11.08%; S, 16.8%.

Found: C, 63.1%; H, 4.44%; N, 10.99%; S, 16.1%.

(4) Poly[4,4'-methylenebis cinnamalthioyl thiosemicarbazone] (PMBCSTSc)

FTIR: 3240, 3036, 2928, 2845, 1606, 1527, 1495, 1412, 1246, 1064, 932, 840 cm^{-1} .

Analysis of $(\text{C}_{20}\text{H}_{17}\text{N}_3\text{S}_3)_n$, calculated: C, 60.7%; H, 4.3%; N, 10.69%; S, 24.3%.

Found: C, 60.28%; H, 4.19%; N, 10.66%; S, 23.9%.

(5) Poly[4,4'-methylenebis cinnamalthioyl meso-stilbenediamine] (PMBCSSt)

FTIR: 3250, 3046, 2926, 1531, 1418, 1366, 1338, 1208, 1199, 1084, 956, 760 cm^{-1} .

Analysis of $(\text{C}_{33}\text{H}_{28}\text{N}_2\text{S}_2)_n$, calculated: C, 76.7%; H, 5.4%; N, 5.4%; S, 12.4%.

Found: C, 76.4%; H, 5.47%; N, 5.32%; S, 17.31%.

RESULTS AND DISCUSSION

Synthesis

Dialdehyde (MBC) was prepared as reported [15] by following a general procedure for the preparation of 5,5'-methylenebis(salicylaldehyde) and 5,5'-methylenebis(2-hydroxyacetophenone) [16,17]. The results of elemental microanalysis also agreed closely with the expected values. The prepared dialdehyde (MBC) was further used to prepare new polythioamides by polycondensation with adducts of diamino compounds, such as ethylenediamine(en), 1,3-propylenediamine (PR), semicarbazide (Sc), thiosemicarbazide (TSc), and meso-stilbenediamine (St) with sulphur in DMAc as a solvent. Each time a solid product was obtained.

Structural formulas of polythioamides were assigned based on Willgerodt-Kindler reaction as proposed [10] and were confirmed by elemental analysis and spectroscopic techniques (Figure 1). The reaction mechanism of polymerization of polythioamide is reported as literature [11].

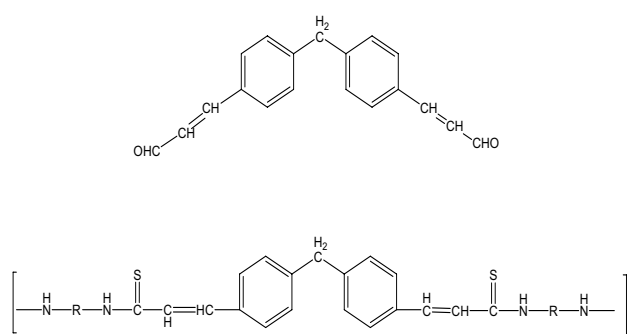


Figure 1. Structure diagrams of: (a) MBC, and (b) its polythioamides. PMBCSen = R = CH_2CH_2 , PMBCSPR = R = $\text{CH}_2\text{CH}_2\text{CH}_2$, PMBCSSc = R = NHCO , PMBCSTSc = R = NHCS , PMBCSSt = R = $\text{CH}(\text{Ph})\text{-CH}(\text{Ph})$.

Table 1. Willgerodt-Kindler type of polycondensation of [4,4'-ethylene bis(cinnamaldehyde)] with sulphur in different solvents: (a) DMF; (b) DMAc; (c) equivalent as elemental sulphur for monomer; (d) insoluble fraction in methanol and soluble in chloroform; and (e) a chloroform insoluble fraction was observed.

Run	Diamine	Solvent	Sulphur ^c element	Yield ^d (%)
1	Ethylenediamine	DMF ^a	2.0	58
		DMF	2.5	89
		DMAc ^b	2.0	66
		DMAc	2.5	92
2	Propylenediamine	DMAc	2.0	69
		DMF	2.5	59
		DMAc	2.5	91
3	Semicarbazide	DMAc	2.5	89
		DMF	3.0	30 ^e
4	Thiosemicarbazide	DMAc	2.5	89
		DMF	3.0	39 ^e
5	Meso-stilbenediamine	DMAc	2.5	91
		DMAc	3.0	79

The effects of reaction condition on the yield percentage for the syntheses of polythioamides were examined. The effects of the amount of elemental sulphur added, solvent of reaction medium, heating time, reaction temperature and the solubility of polythioamides were examined. The addition of elemental sulphur was varied from 2.0, 2.5, to 3.0 milliequivalent, but better results were obtained with addition of 2.5 milliequivalent of elemental sulphur. The solvents DMAc, DMF, o-xylene and dimethylene glycol were examined as solvents for formation of polythioamides. Better yield was obtained with DMAc

and was selected (Table 1). Heating time of reaction mixture at 115°C was varied for 6, 12, 18, and 20 h. The maximum yield was obtained by heating for 18 h and was selected. Solubilities of dialdehyde MBC and its polythioamides were examined in water, methanol, ethanol, acetone, butanol, chloroform, THF, DMF, DMSO, and DMAc. Dialdehyde and polythioamides were insoluble in water, methanol and ethanol, partially soluble in butanol, but soluble in acetone, chloroform, THF, DMF, DMSO, and DMAc (Table 2). Solvents with high dielectric constant THF, DMF, and DMAc were preferred as

Table 2. Solubilities of dialdehyde (MBC) and their polythioamides.

Sample	Compound	Solubility in different solvents						
		H ₂ O	Ethanol	Butanol	Acetone	CHCl ₃	THF	DMF
1	MBC	-	-	±	+	+	+	+
2	(PMBCSen) _n	-	±	+	+	+	+	+
3	(PMBCSPR) _n	-	±	+	+	+	+	+
4	(PMBCSSc) _n	-	±	±	+	‡	‡	+
5	(PMBCSTSc) _n	-	±	±	‡	‡	‡	+
6	(PMBCSSt) _n	±	+	‡	‡	‡	+	‡

(‡) Very soluble, (+) soluble, (±) partial soluble, (-) insoluble

solvents.

IR spectrum of MBC indicated strong bands at 1682 cm^{-1} due to $\nu\text{C}=\text{O}$ vibrations of aldehyde. When

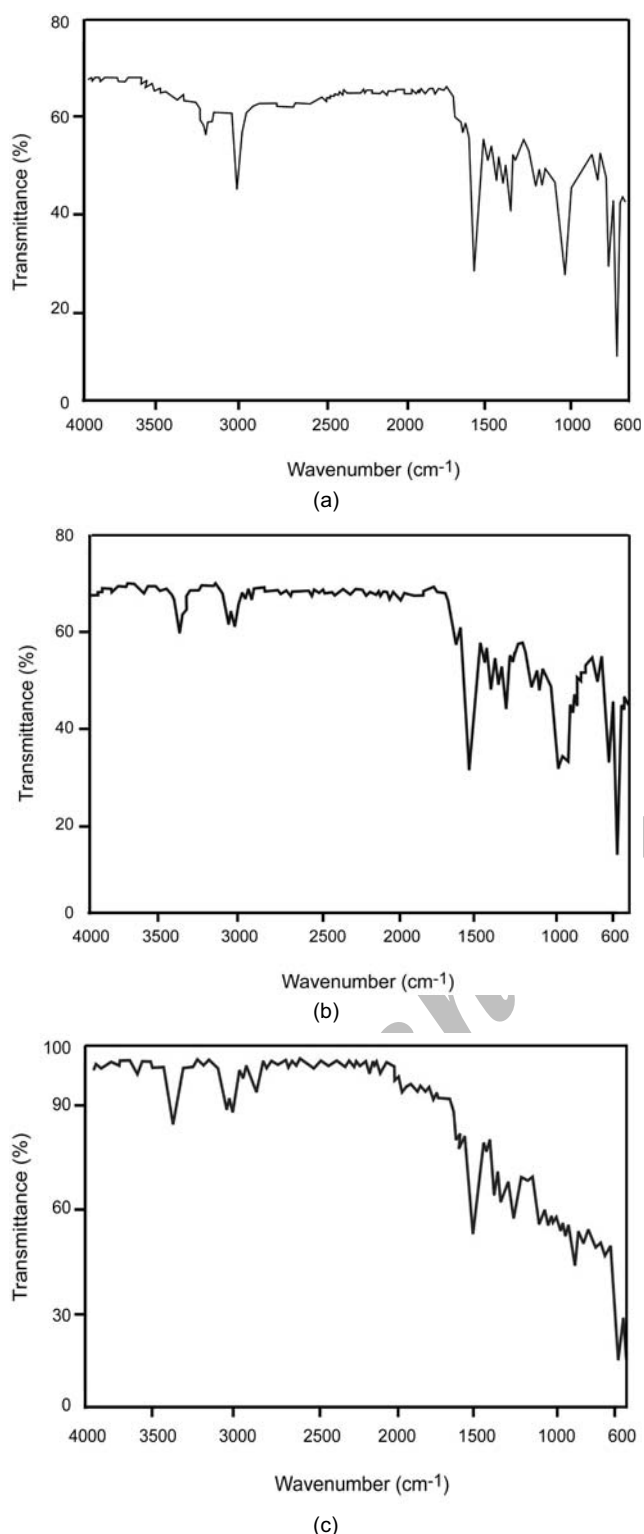


Figure 2. FTIR spectra of MBC (a), PMBCSen (b) and PMBCSPR (c).

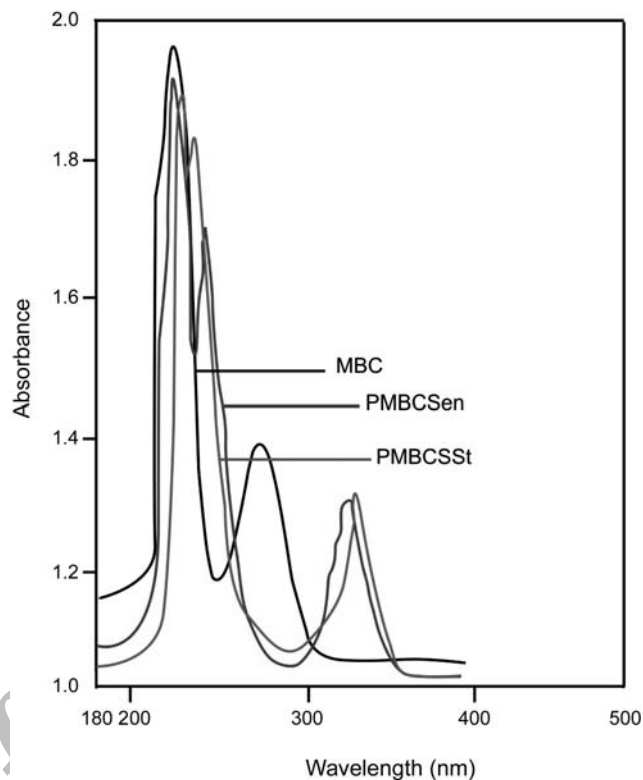


Figure 3. Absorption spectra of MBC, PMBCSen and PMBCSSt.

aldehyde reacts with diamines then absorption of infrared radiation causes covalent bonds within the molecule to be promoted from one vibrational energy level to high energy level. Therefore aldehydic band in the polythioamides PMBCSen, PMBCSPR, meso-PMBCSSt, and PMBCSTSc was either absent or observed only as weak bands due to polycondensation (Figure 2). The polymer PMBCSSc indicated strong bands at 1654 cm^{-1} due to the presence of $\nu\text{C}=\text{O}$ groups, contributed by semicarbazide. All the polythioamides indicate a characterized band within $3200\text{--}3300\text{ cm}^{-1}$ due to $\nu\text{N-H}$ vibrations and polythioamides also indicated a band within $1230\text{--}1260\text{ cm}^{-1}$ for $\nu\text{C}=\text{S}$ vibrations. The dialdehyde MBC and its polythioamides indicated two to three bands within $1578\text{--}1395\text{ cm}^{-1}$ due to the aromatic ring and $\nu\text{C}=\text{C}$ vibrations.

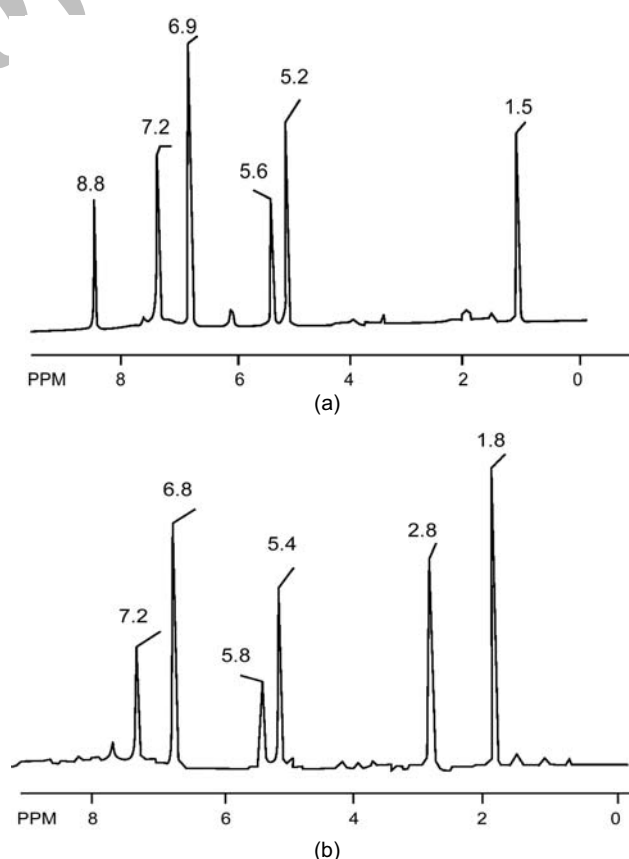
The measurements of UV/Vis spectra were carried out in DMF and THF. Dialdehyde MBC indicates two absorption bands at 262 nm and 338 nm with the molar absorptivity of 2.3×10^4 and $1.0 \times 10^4\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ due to $\pi\text{-}\pi^*$ transition within $\nu\text{C}=\text{C}$

Table 3. UV/Vis data of MBC and Schiff base polythioamides.

Sample	Compound	λ_{\max} (nm)	ϵ	Solvent
1	MBC	262	23490 L/mol.cm	DMF
		338	10224 L/mol.cm	
2	(PMBCSen) _n	271	383	DMF
		386	220	
		410	195	
3	(PMBCSPR) _n	266	372	DMF
		388	165	
		418	122	
4	(PMBCSSC) _n	272	370	DMF
		392	268	
		412	112	
5	(PMBCSTSc) _n	275	386	DMF
		395	245	
		420	210	
6	(PMBCSSt) _n	246	395	THF
		290	314	
		348	265	

transition in the benzoid rings and conjugated carbonyl groups ($\nu\text{C}=\text{O}$), respectively. The polythioamides indicate three bands within 241-418 nm (Figure 3). The observation of a new band or a shift in the position of the band as compared to MBC may be due to $\pi\text{-}\pi^*$ transition owing to incorporation of conjugated thio groups ($\nu\text{C}=\text{S}$) with $\nu\text{C}=\text{C}$ bonds of benzoid rings in the polythioamides (Table 3).

The ^1H NMR spectra of dialdehyde and polythioamides were recorded (Figures 4a and 4b). The ^1H NMR spectra of dialdehyde showed a peak of aldehyde group at $\delta = 8.8$ due to proton attached to aldehyde group. In ^1H NMR spectrum of polythioamide, the ratios of the peaks area agree with the suggested assignment and no peak attributed to aldehyde group is observed. But new peak was observed at $\delta 2.8$ due to $\text{N-CH}_2\text{-}$ and supports the formation of polythioamides. MBC and polythioamides indicated peaks within the range of $\delta 7.2\text{-}6.8$ due to aromatic nature of the compounds. The unsaturated part of compound can be attributed within the range of $\delta 4.9\text{-}5.9$, while the methylene group at $\delta 1.2\text{-}1.8$ was observed in different polythioamides. In the ^{13}C NMR spectrum of polythioamide, a characterized peak attributed to the thiocarbonyl group ($\text{C}=\text{S}$) is

**Figure 4.** ^1H NMR spectra of: (a) MBC, and (b) Schiff base polythioamide PMBCSen.

observed at δ 198-199, with other attributions.

Thermal Properties

Thermoanalytical studies were carried out in nitrogen atmosphere between room temperature and 600°C. The weight loss in case of MBC started at 220°C and 100% weight loss was observed at 480°C, whereas in polythioamides weight loss started within 150-300°C and 80% to 90% weight loss occurred up to 600°C (Figures 5a and 5b).

The viscosity measurements of dialdehyde MBC and newly synthesized polythioamides formed were recorded within 283-323 K with concentration within 0.02-0.08 g/dL in THF. The relationship between the reduced viscosity (η_{red}) and concentration was observed linear for all the compounds and an increase in reduced viscosity was observed with an increase in concentration and decrease in temperature (Figure 6). Intrinsic viscosity (η) is a function of molecular mass

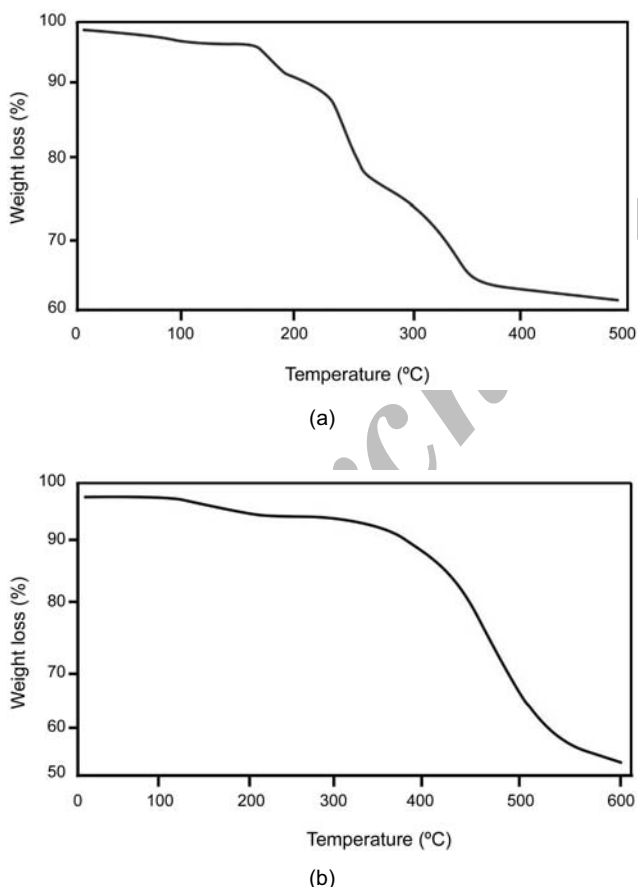


Figure 5. TGA curves of MBC with 10 mg of sample, with a heating rate of 15°C/min and nitrogen flow rate of 50 mL/min (a), and PMBCSen with 15 mg of sample (b).

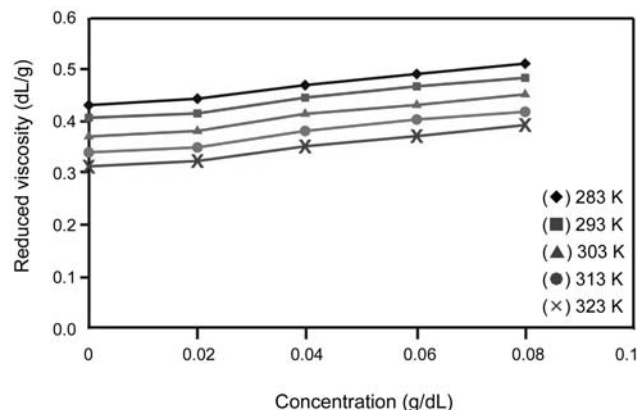


Figure 6. Plot of reduced viscosity against concentration of PMBCSen at different temperatures.

and it increased with increase in the molecular mass of polymer. Intrinsic viscosity (η) of the MBC was observed within 0.1869 to 0.2489 dL/g and polythioamides PMBCSen, PMBCSPR, PMBCSSc, PMBCSTSc, PMBCSSt indicated within 0.393-0.473 dL/g, 0.407-0.488 dL/g, 0.2471-0.437-0.509 dL/g, 0.2673-0.435-0.514 dL/g and 0.443-0.5201 dL/g, respectively. The polythioamides indicated higher values of intrinsic viscosities than MBC (Table 4) and support the formation of polythioamides. The absolute viscosity (η_{abs}) for MBC was observed within 0.1910-0.4352 mNs/m² as compared to polythioamides PMBCSen, PMBCSPR, PMBCSSc, PMBCSSt, and PMBCSTSc were within 0.4541-0.5001, 0.4612-0.599, 0.485-0.602, 0.5162-0.6117 and 0.5281-0.653 mNs/m², respectively. Absolute viscosity increased with concentration, due to the increase in the density of solution and possible formation of associates, whereas a decrease in η_{abs} was observed with increase in temperature. All thermodynamic parameters of dilute solution of dialdehyde and polythioamides were calculated in THF. The values of ΔG_v for MBC were within 11.989-14.1287 kJ.mol⁻¹ as compared to the polythioamides PMBCSen 12.28-14.615 and PMBCSPR 13.126-14.63 kJ.mol⁻¹. The values of ΔG_v for dialdehyde and their polythioamides increased with an increase in temperature as well as concentration. The value of ΔG_v increases with increase in temperature which indicated that shape transition of the polythioamide molecules takes place during flow process. The values of ΔH_v for dialdehyde were 11.505-11.69 kJ.mol⁻¹

Table 4. Intrinsic viscosity of MBC and Schiff base polymers in THF.

Compound	[η] (dL/g)				
	283 K	293 K	303 K	313 K	323 K
MBC	0.2489	0.2190	0.1999	0.1869	0.1739
(PMBCSen) _n	0.4730	0.4530	0.4330	0.4130	0.3930
(PMBCSPR) _n	0.4883	0.4680	0.4480	0.4280	0.4080
(PMBCSSc) _n	0.5084	0.4884	0.4690	0.4480	0.4270
(PMBCSTSc) _n	0.5150	0.4940	0.4720	0.4540	0.4350
(PMBCSSt) _n	0.5201	0.5030	0.4810	0.4620	0.4430

as compared to the polythioamides PMBCen (8.604-8.771 kJ.mol⁻¹) and PMBCSPR (7.952-8.11 kJ.mol⁻¹). The values of ΔH_v increased with an increase in the concentration because more energy is required to overcome the flow of polymeric solution. However the values of ΔH_v of viscous flow are less dependent on temperature, maybe the polythioamides are less cross-linked in THF. Similarly a decrease in the value of ΔH_v was observed in polythioamides as compared to dialdehyde (MBC). It may be because of aggregation of the molecules in polythioamides. The values of ΔS_v of MBC were -0.0013 to -0.0081 J/K as compared to their polythioamide (PMBCSen) ranged from -0.0112 to -0.0197 J.K⁻¹. The negative sign of ΔS_v for polythioamides shows that during flow, the molecules are becoming more extended due to the uncoiling of the polymer molecules taking place in the solution.

CONCLUSION

The Willgerodt-Kindler type of polycondensation is one-pot three-component reaction of dialdehyde and diamines with sulphur and resulted in the formation of several polythioamides in moderate to good yields. These obtained polythioamides indicated good thermal stability up to 600°C for 80-90% weight loss. The polythioamides indicated solubility in organic solvents such as chloroform, acetone THF, DMF, DMAc, and DMSO, because all these aromatic polythioamides are amorphous in nature. The intrinsic viscosities of these polythioamides range within 0.393-0.5201 dL/g.

REFERENCES

1. Gressier JC, Levesque G, Aliphatic polythioamides and study of some physio chemical properties, *Eur Polym J*, **16**, 1167-1173, 1980.
2. Levesque G, Gressier J-C, Room temperature synthesis and characterization of aliphatic polythioamides, *Polym Sci Polym Lett Ed*, **17**, 281-285, 1979.
3. Deletre M, Levesque G, Polythioamide synthesis through chemical modification of polyamides, *Macromolecules*, **23**, 4876-4880, 1990.
4. Delfanne I, Levesque G, Polythioamides and poly(1,3,4-thiadiazole) synthesis from dimethyl tetrathioterephthalate, *Macromolecules*, **22**, 2589-2592, 1989.
5. Gressier J-C, Levesque G, Aromatic polythioamides, synthesis and study of thermal and solution behaviour, *Eur Polym J*, **17**, 695-706, 1981.
6. Tabak G, Pham T-N, Levesque G, Synthesis and characterization of naphthalene containing polythioamides, *Polymer*, **39**, 5561-5566, 1998.
7. Deletre M, Levesque G, Kinetics and mechanism of polythioamidation in solution, I. Reaction of mono- and bis(dithioester)s with excess amine, *Macromolecules*, **23**, 4733-4741, 1990.
8. Amupitan J, Oxidation and reduction, *Org Synth*, **730**, 1983.
9. Kawai Y, Kanbara T, Hasegawa K, Preparation of polythioamides from dialdehyde and 4,4'-trimethylenedipiperidine with sulfur by the Willgerodt-Kindler reaction, *J Polym Sci Part A:*

- Polym Chem*, **37**, 1737-1740, 1999.
10. Kanbara T, Kawai Y, Hasegawa K, Morita H, Yamamoto T, Preparation of polythioamides from dialdehydes and diamines with sulfur by the Willgerodt-Kindler type reaction, *J Polym Sci Part A: Polym Chem*, **39**, 3739-3750, 2001.
 11. Kagaya S, Sato E, Masore I, Hasegawa K, Kanbara T, Polythioamide as a collector for valuable metals from aqueous and organic solutions, *Chem Lett*, **32**, 622-623, 2003.
 12. Hadjikakou SK, Ozturk II, Xanthopoulou MN, Zachariadis PC, Zartilas S, Karkabounas S, Hadjiliadis N, Synthesis, structural characterization and biological study of new organotin (IV), silver (I) and antimony (III) complexes with thioamides, *J Inorg Bio*, **102**, 1007-1015, 2008.
 13. Lobana TS, Sultana R, Hundal G, Hetrocyclic compounds also able to form copper complexes with 1,3-imimidazoline-2-thio(ones) in the presence of triphenylphosphine, *J Polyhedron*, **27**, 1008-1016, 2008.
 14. Mills WH, Quibells TH, *J Chem Soc*, 843, 1935.
 15. Khuhawar MY, Shah A, Mughal MA, Synthesis and characterization of some new Schiff base polymers, *Chin J Polym Sci*, **25**, 399-407, 2007.
 16. Khuhawar MY, Channer AH, Shah SW, Synthesis and thermoanalytical studies of some Schiff base polymers and their metal chelates, *J Chem*, **22**, 14-17, 2000.
 17. Khuhawar MY, Channer AH, Shah SW, Synthesis and thermoanalytical studies of some Schiff base polymers derived from 5,5'-methylenebis(2-hydroxy acetophenone), *Eur Polym J*, **34**, 133-135, 1998.