Sindh Univ. Res. Jour. (Sci. Ser.) Vol.45 (1):153-1158 (2013)

SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)

One Pot Synthesis and Characterization of Derived Polythioamide with 1, 2-Phenylenediamine

A. SHAH[++], M. Y. KHUHAWAR, H. KHAN, A. A. SHAH*

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

Received 12th January 2013 and Revised 18th February 2013

Abstract: 1, 2- Phenylenediamine a weak aromatic amine reacted with dialdehyde by Willgeordt kindler type reaction to form polythioamide. Dialdehyde 4, 4'- methylene bis(cinnamaldehyde) (MBC) contains conjugated double bonds with aldehydic groups which formed polythioamides in the presence of elemental sulfur, with diamino compounds. The derived polythioamide (PMBCSPh) was characterized by C. H. N analysis, spectroscopic techniques, thermal analysis and viscosity measurements. The synthesized polythioamide indicated loss in weight up to 600 ºC. The dialdehyde (MBC) and its derived polythioamide were soluble in various organic solvents like acetone, chloroform, tetrahydrofuran, dimethylformamide, dimethylacetamide, and dimethylsulphoxide. The intrinsic viscosities ranged within 0.284- 0.341 dL/g for (PMBCSPh) within 283K- 323K, as compared to 0.174- 0.249 dL/g for dialdehyde (MBC) in THF.

Key words: Polythioamide, U/V-Visible Spectroscopy, I.R Spectroscopy, Thermal Studies.

1. INTRODUCTION

1, 2-Phenylenediamine is a weak aromatic base and important precursor to many heterocyclic compounds. It is isomeric with m-phenylenediamine and p-phenylenediamine, but o-phenylenediamine is about 1000 times less toxic than the para-isomer. 1, 2-Phenylenediamine condenses with ketones or aldehydes to give rise to a variety of useful products.

A wide variety of structurally related polythioamide has been synthesized by Willgeordt-kindler type reaction. Polythioamides are stable like polyamides in which C = O group has been replaced by C = S, but the melting points of polythioamides are decreased about 50- 80 ºC than homologous polyamides (Levesque, *et. al.* 1978); (Gressier, *et.al.* 1980). As polythioamides contain thiocarbonyl groups in their structure, which decrease the hydrogen bonding and may enhance solubility in highly polar solvents like chloroform (Deletre, *et. al.* 1983).

The Willgeordt-Kindler reaction is one of famous reaction for the synthesis of thioamides (Kawai, *et. al.* 1999) and polythioamides formed from dialdehyde with different diamines in the presence of sulphur by coupling polycondensation reaction. Heteroaromatic dialdehyde gave polythioamides in moderate yields but diketones gave no polymeric product due to the slow dehydration of amines with diketones (Kanbara, *et. al.* 2001).

Several polythioamides were prepared from aromatic dialdehyde and different diamines and they exhibited unusually good resistance to decomposition by heat (Kagaya, *et. al.* 2003), (Shah, *et. al.* 2009). Recently, some polythioamides were synthesized, characterized and used for different purposes like some in biological study of new organotin (IV), (Hadjikakou, *et. al.* 2008) silver (I) and antimony (III) and some work as adsorbent resins for metals (Lobana, *et. al.* 2008) (Shah, *et. al.* 2012).

The present work examines the formation of a new polythioamide from 4, 4'-methylenebis (cinnamaldehyde) with 1,2-phenylenediamine by Willgeordt kindler type reaction, in the presence of elemental sulfur and confirmed by the help of various spectroscopic techniques.

2. EXPERIMENTAL

Materials

Cinnamaldehyde, urea, 1,2-phenylenediamine (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.

Apparatus

The data of elemental micro-analysis was taken from Elemental Micro-Analysis Ltd, Devon, U.K. The I.R spectra were taken on a Nicolet Avatar 330 FTIR (Thermo Nicolet Electron Corporation, USA) with attenuated total reflectance (ATR) accessory within 4000-600 cm^{-1}. Dimethylformamide (DMF) and tetrahydrofuran (THF) were used as a solvents for spectroscopic studies on a double beam Hitachi 220

++Corresponding Author: A. SHAH e. mail: anashba_shah@yahoo.com Tel 022-2772325 Fax no: 92222771373.

* Mehran University Institute of Science and Technology Development, Jamshoro.

spectrophotometer (Hitachi (Pvt) Ltd, Tokyo, Japan), with dual 1 cm silica cuvettes within 185-700 nm. Thermogravimetry (TG) and differential thermal analysis (DTA) were obtained on Pyris Diamond TG/DTA (Perkin Elmer, Japan) from room temperature to 600 ^{o}C. The heating rate of (PMBCSPh) was taken 15 ^{o}C/ min with nitrogen flow rate (50 mL/ min). An amount of 10 mg of the sample was placed in platinum crucible and recorded against a-alumina as reference.

The viscosity results of dialdehyde (MBC) and its polythioamide (PMBCSPh) were noted within temperatures 283-323 K with interval of 10 K with the help of a Technico ASTM 445 suspended level viscometer. Every time 15 mL of solution was consumed and at least three readings were taken as an average flow time under the same conditions. A gallenkamp viscometer bath was taken to control the temperature.

Synthesis of Dialdehyde 4, 4'- Methylene Bis (Cinnamaldehyde):

The dialdehyde of [4, 4'- methylenebis (cinnamaldehyde)] was prepared and purified by reported procedure (Shah, *et. al.* 2009).

Synthesis Of Polythioamide From 4, 4'- Methylene Bis (Cinnamaldehyde):

(2 mmol) 1,2–phenylenediamine dissolved in THF (3 mL) was added sulphur (160 mg), dimethylacetamide (DMAc) (10 mL) at room temperature. The reaction mixture was turned dark green after 10 min with continuous stirring. Introduced (2 mmol) dialdehyde (MBC) in (10 mL) of DMAc and added to the reaction mixture at 115ºC. The mixture was refluxed about 18 h in N_2 atmosphere. After heating, added (100 mL) methanol in mixture and precipitation were formed which were separated by simple filtration. Crude ppt was extracted with $CHCl_3$ (50 mL) then concentrated upto (8 mL). the concentrated mixture poured in (20 mL) methanol with the reformation of pure percipitates. Again precipitations were filtered and rinsed with CH_3OH and CS_2 to remove all impurities.

Poly[4,4'-methylene(biscinnamalthioyl)1,2-phenylenediamine] (PMBCSPh)

FT IR: 3230, 3048, 2940, 1595, 1500, 1248, 1112, 1044, 1026, 787, 742 cm^{-1}.

Analysis of $(C_{24}H_{20}N_2S_2)n$, calculated: C, 78.26 %; H, 5.43 %; N, 7.60 % ; S, 8.69 %.

Found: C, 78.21 %; H, 5.46 %; N, 7.57 %; S%; 8.61.

3. RESULTS AND DISCUSSION

The data of elemental micro-analysis were about to equal with the estimated results. The dialdehyde (MBC) was used to prepare newer polythioamide by polycondensation with 1,2-phenylenediamine, in the presence of elemental sulfur. The structures of MBC and its derived polythioamide are shown in **(Fig. 1).** The solubility of MBC and polythioamide (PMBCSPh) were examined in different organic solvents such as acetone, butanol and chloroform THF, DMF, DMSO but polythioamide completely dissolved in THF, DMF and dimethylsulphoxide (DMSO)**.** Therefore the solvents with high dielectric constant are preferred for the polythioamide.

The dialdehyde (MBC) and polythioamide were characterized by IR spectroscopy. There was a clear difference among IR spectra of dialdehyde and polythioamide. IR spectrum of the MBC gave strong bands at 1730 and 1700 cm^{-1}, related to υC=O vibrations. The corresponding band in spectrum of the polythioamide (PMBCSPh) was absent due to polycondensation**.** Polythioamide (PMBCSPh) give a characterized band at 3230 cm^{-1} as a result of νN-H vibrations and at 1248 cm^{-1} due to νC=S vibrations **(Fig. 2)**. The dialdehyde (MBC) gave one absorption bands at 262 nm with molar absorptivity 2.3 × 10^4 L·mol^{-1}·cm^{-1} and second at 338 nm with the molar absorptivity 1.0 × 10^4 L·mol^{-1}·cm^{-1}. Both absorption bands appeared in dialdehyde as well as polythioamide. But polythioamide also indicated third band due to conjugated thio groups (υC=S-C=C) of benzoid rings in the polythioamide **(Fig. 3)**. Thermoanalytical studies were carried out in nitrogen atmosphere from room temperature to 600ºC. The weight decomposition of MBC started at 180ºC and 100% loss was observed up to 600ºC, but in polythioamide (PMBCSPh) weight loss occurred within 212−587ºC and 82% weight loss observed up to 600ºC (**Fig. 4).**

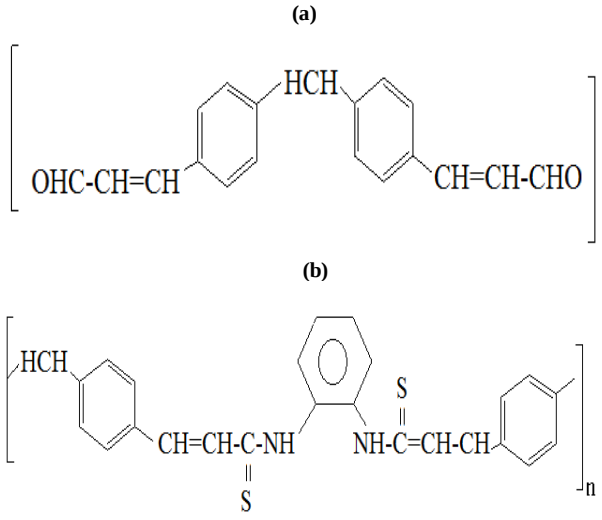


Fig 1: Structure diagrams of: (a) MBC, and (b) derived polythioamide (PMBCSPh)

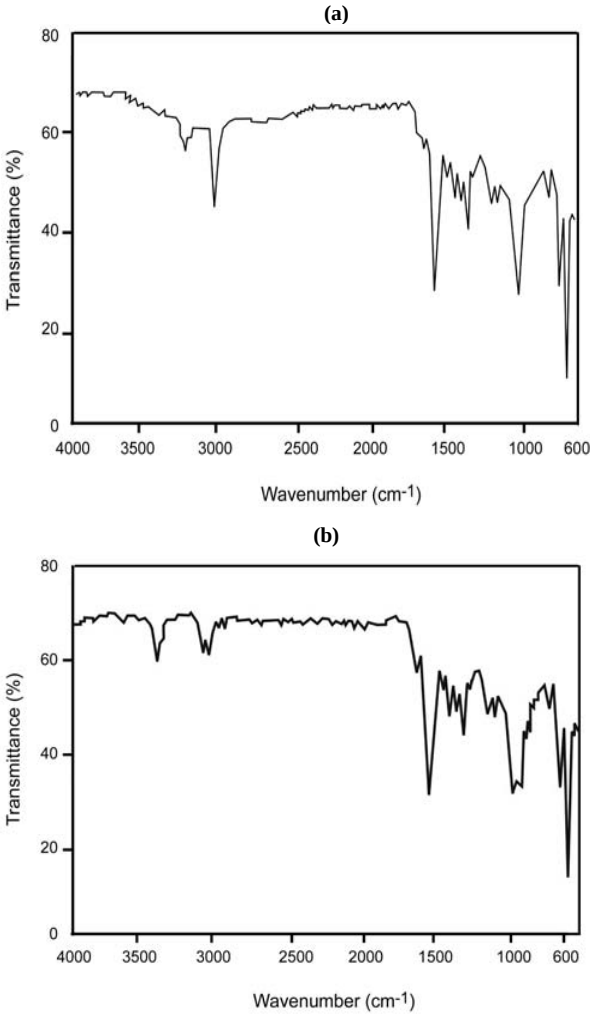


Fig 2: FTIR spectra of (a) MBC and (b) polythioamide PMBCSPh.

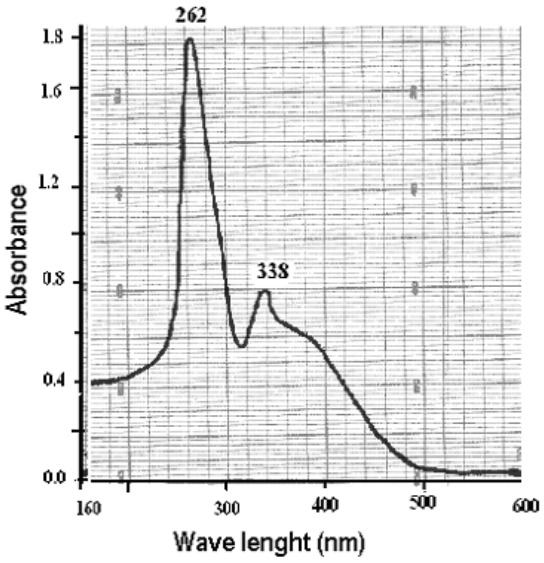


Fig: 3(a): U/V-Vis Spectrum for dialdehydes of (MBC)

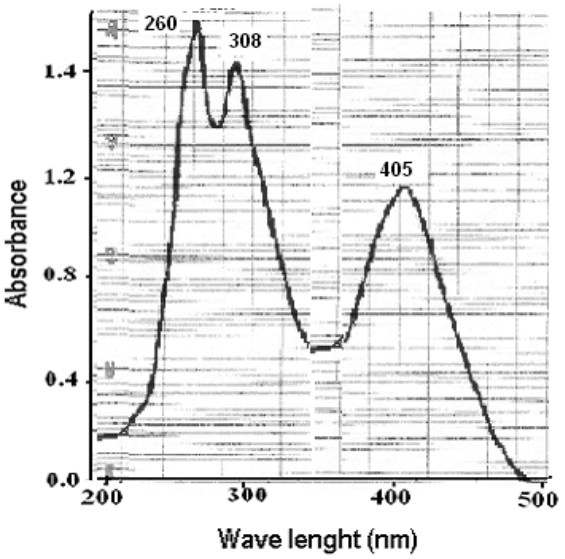


Fig: 3(b): U/V-Vis Spectra for (a) (MBC) (b) polythioamide (PMBCSPh).

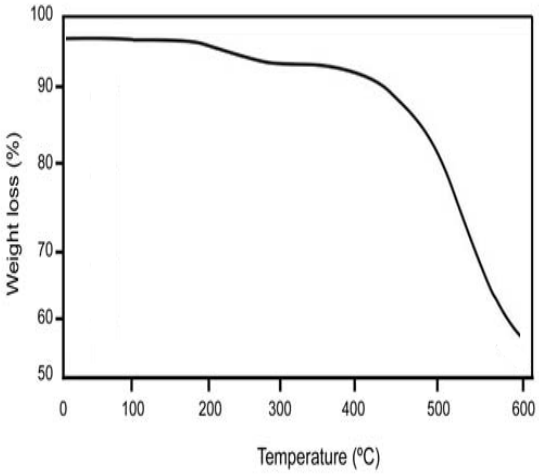


Fig. 4: TGA curves of 4,4'-metylenebis(cinnamalthioyl) 1,2-phenylenediamine obtained with a heating rate 10 K/min and nitrogen flow rate of 50 mL/min.

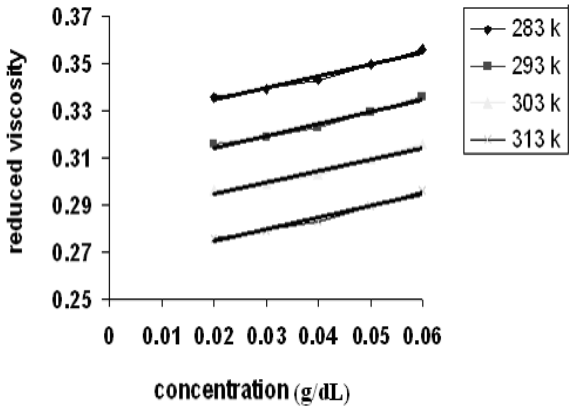


Fig: 5: Reduced viscosity v/s concentration of polythioamide (PMBCSPh) at different temperature.

The viscosity measurements of dialdehyde MBC and the polythioamide were recorded within 283 to 323 K. The intrinsic viscosity of the MBC was observed within 0.1869 to 0.2489 dL/g, while that of the polythioamide (PMBCSPh) in the range 0.264−0.324 dL/g. The relationship between reduced viscosity and concentration in the range of 0.02 to 0.08 g/dL was linear for all the compounds, and an increase in reduced viscosity was observed with increase in the concentration and decrease with temperature **(Fig. 5).** The polythioamide indicated higher values of intrinsic viscosity than that of dialdehyde MBC and these results also support the formation of the polymerization. Absolute viscosity improved with concentration due to the increase in density of solutions **(Table: 1)**. The absolute viscosity (ηabs) decreased with decrease in density at higher temperatures. All thermodynamic parameters of dilute solutions of dialdehyde and polythioamide were obtained in THF. The values of ΔGv for dialdehyde were 12.0−14.1 kJ mol^{-1} as compared to the polythioamide (PMBCSPh) 14.27-14.59 kJ mol^{-1}. The value of ΔGv for dialdehyde and its polythioamide increased at higher temperature as well as concentration. The free energy of activation (ΔGv) increase on raising the temperature, represented shape changing in polythioamide **(Table: 2).** The values of ΔHv for dialdehyde were 11.5−11.7 kJ mol^{-1} higher than polythioamide (PMBCSPh) (7.95−8.11 kJ mol^{-1}). The results of ΔHv increased with increase in concentration because more energy was required to overcome the force of attraction among the molecules themselves during their flow. However the values of ΔHv of viscous flow are less dependent on temperature, may be the polythioamides are less cross linked in THF. A lower value of ΔHv was observed in polymeric compound as compared to that of dialdehyde (MBC), possibly, because of the aggregation of polymeric molecules. The values of ΔSv of MBC were from −0.0013 to −0.0081 J/K, while those of the polythioamide (PMBCSPh) were in the range of −0.0112 to −0.0197 J/K. The negative sign of entropy (ΔSv) for polythioamide indicates that during flow the molecules are more suitable to extend because of the uncoiling shape of the molecules in the solution.

Table: 1: Absolute viscosity of derived polythioamide (PMBCSPh) at different temperature (m.N.S/m^2)

Concentration (g/dL)	Temperature (K)			
	283	293	303	313
0.02	0.474	0.376	0.278	0.188
0.04	0.486	0.388	0.290	0.192
0.05	0.492	0.394	0.296	0.198
0.06	0.502	0.404	0.306	0.208

Table: 2: Free energy of activation of viscous flow (ΔG_v) for (PMBCSPh) at different temperature. (K. J. mol^{-1}).

Concentration (g/dL)	Temperature (K)			
	283	293	303	313
0.02	13.78	14.35	14.57	14.59
0.03	13.87	14.43	14.61	14.62
0.04	14.09	14.54	14.72	14.70
0.05	14.13	14.58	14.74	14.72
0.06	14.27	14.68	14.81	14.78

4. CONCLUSIONS

The work reports the synthesis of polythioamide by Willgeordt kindler type of reaction. The synthesis of the polythioamide (PMBCSPh) was confirmed by elemental microanalysis, IR, UV and Vis spectroscopy, thermogravimetric analysis and viscosities measurements. The polythioamide indicated solubility in common solvents including chloroform, acetone tetrahydrofuran and dimethyl formamide.

REFERENCE:

Amupitan, J. (1983) Oxidation and reduction. Org. Synth. 730.

Ambreen, S., M. Y. Khuhawar. and A. S. Asif, (2009) Preparation and Characterization of Schiff Base Polythioamides Derived from [4,4'-Methylenebis (cinnamaldehyde)] by Willgerodt-Kindler Reaction. Iran. Polym. J. 18 **(3):** 217-225.

Ambreen, S., M. Y. Khuhawar., and A. S. Asif, (2012) Evaluation of sorption behavior of polymethylene-bis (2-hydroxybenzaldehyde) for Cu(II), Ni(II), Fe(III), Co(II) and Cd(II) ions. Iran. Polym. J. **(21):** 325– 334.

Deletre, M., and G. Levesque, (1990) Polythioamide synthesis through chemical modification of polyamides. Macromolecules **(23):** 4876- 4880.

Gressier, J. C., and G. Levesque, (1980) Aliphatic polythioamides and study of some physio chemical properties. Eur. Polym. J. 16: 1167- 1173.

Hadjikakou, S. K., I. I. Ozturk., M. N. Xanthopoulou., P. C. Zachariadis., S. Zartilas., S. Karkabounas., and N. Hadjiliadis, (2008) Synthesis, structural characterization and biological study of new organotin (IV), silver (I) and antimony (III) complexes with thioamides. J. Inorg. Bio. **(102):** 1007- 1015.

Kawai, Y., T. Kanbara and K. Hasegawa, (1999) 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.

Kanbara, T., Y. Kawai., K. Hasegawa., H. Morita, and T. Yamamoto, (2001) Preparation of polythioamides from dialdehydes and diamines with sulfur by the Willgeordt-Kindler type reaction. J. Polym. Sci Part A. Polym. Chem. **(39):** 3739-3750.

Kagaya, S., E. Sato., I. Masore., K. Hasegawa and T. Kanbara, (2003) Polythioamide as a collector for valuable metals from aqueous and organic solutions. Chem Lett, **(32):** 622- 623.

Levesque, G., and J. C. Gressier, (1979) Room temperature synthesis and characterization of aliphatic polythioamides. Polym. Sci. Polym. Lett Ed, **(17)**: 281-285.

Lobana, T. S., R. Sultana, and G. Hundal, (2008) Hetrocyclic compounds also able to form copper complexes with 1,3-immidazoline-2-thio(ones) in the presence of triphenylphosphine. J. Polyhedron. **(27):** 1008- 1016.