Pak. j. sci. ind. res. Ser. A: phys. sci. 2023 **66A**(1) 1-6

A New Method of Synthesis of Polythiols Schiff Base with Sulphur and Azomethine Donors and their Characterizations by Willgeordt Kindller

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(received August 24, 2021; revised March 18, 2022; accepted March 29, 2022)

Abstract. Some new polythiols were derived from aromatic aldehyde (2-hydroxy benzaldehyde) and different diamines (semicarbazide, 4-phenyl, 3-thiosemicarbazide, 4-4′-oxydianiline and N, N′- dimethyl *p*-phenylenediamine), in the presence of elemental sulphur.The process of condensation is carried out by the Willgerodt Kindler (WK) reaction of azomethine donor or derivatives with elemental sulphur in the presence of a strong base as a catalyst. The polythiols (polythioamides) were characterized by different techniques like elemental micro analysis, FTIR, UV- Vis spectroscopies, thermal analysis and viscosity measurement. The FT-IR showed the main band around 1235-1265/cm^{-1} because of the formation of thiol groups in respected polythiols to *v*C=S vibrations. The polythiols indicated improved thermal solidity up to 600 ºC. These polythiols were soluable in highly polar organic solvents due to their complex structures. The intrinsic visco-metrical data of these polythiols reached about 0.393-0.5201 dL/g in THF.

Keyword: polythiols, synthesis, Willgerodt Kindler (WK) reaction, FT-IR, TG/DTA, enthalpy

Introduction

Polythiols schiff bases are the type of polyamides, which have been used in the field of medical and organic chemistry, 1,2 aromatic thioamides have been remarkable importance in the preparation of biologically based five and six-membered heterocycles (Hossein, 2020; Demetgül *et al*., 2012; Shalin *et al*., 2009). Thioamides also involved in synthetic chemistry, transition metal coordination chemistry and material chemistry (Torbus *et al*., 2021).

The Willgerodt Kindler (WK) type of reaction (Aghapoor *et al*., 2007; Kawai *et al*., 1999) is adaptable synthetic process, which is used for the research of polythiols as it is a simple and one pot method. Therefore, all the components like aldehyde, diamine and sulphur would be introduced in one reaction simultaneously.

The Willgerodt-Kindler (WK) reaction is very famous reaction for the synthesis of thioamide derivatives (Shah *et al*., 2014; 2009; Deletre, 1990). Although, there has been very less information for the synthesis thioamides such as thio-benzanilide, using WK reaction and the results also depend on some specific reaction conditions or microwave techniques (Zhanwei *et al*., 2016; Deletre, 1990). Thio-benzanilide and its derivatives have been usually formed Lawson’s reagent.

To dissolve the limitation of the WK reaction, we have modified the reaction conditions along with the addition of a catalytic amount of a particular base, for the preparation of thiols schiff base (Kagaya, 2003; Kanbara *et al*., 2001). Mostly, the addition of base is necessary recommended in the Willgerodt Kindler method.

Polythiols schiff bases are stable dimers/ oligomers, like amides, where carbonyl group replaced into thiol group due to the involvement of sulphur, although it has lesser M.P as compared to corresponding amides. Aromatic polythiols schiff bases are possibly motivating constituents as having reduced M.P, lower glass transition temperatures and improved solubility in polar solvents (Hadjikakou *et al*., 2008; Lobana *et al*., 2008).

Thiols and polythiols schiff bases are widely used as resin, in metal uptake studies. On the other hand, thiol compounds have also shown good biological activities containing antibacterial and antifungal than amide compounds. Therefore, thiol have importance in the medicinal and pharmaceutical fields (Shah *et al*., 2017; Khuhawar *et al*., 2007; 2000). As subsequent thiol schiff base possesses elemental sulphur and azomethine groups in such a way that the coordination covalent bond formed very effectively with metals (Ismail *et al*., 2020; Ghulam, 2017).

Present work describes a pot synthesis of schiff base polythiols from bis(2-hydroxy benzaldehyde) with

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different Azomethine donors groups like semicarbazide, 4-phenyl 3- thio semicarbazide, 4-4′-oxydianiline and N, N′- dimethyl *p*-phenylenediamine. The work also examined the C.H. N analysis for the complete synthesis of polythiols. All spectroscopic and thermal data have been observed very clearly. The polythiols also exhibits certain thermodynamic results which give the valuable information about the bonding structure of polythiols.

Meterial and Methods

Instrument. This synthesis of both schiff base polythiols were confirmed by C.H.N elemental micro-analysis, which was carried out by elemental micro-analysis lab, London. Determinations of schiff base polythiols were carried out using the Varian spectra AA.20 atomic absorption spectrophotometer. FTIR-Spectra were recorded on Nicolet Avatar 330 FT-IR with total attenuated reflectance (ATR) attachment around 4000-600 cm^{-1}. Spectrophotometer results were taken by using double beam Hitachi 220 spectrophotometer (Hitachi (Pvt) Tokyo, Japan) through dual 1 cm silica cuvettes,ranged 185-700 nm. Thermogravimetry (TG) was observed on Pyris Diamond TG / DTA (Perkin Elmer, Japan) upto 600 °C with a heating rate 15 °C /min and nitrogen flow rate 50 ml/min and flow rate of nitrogen was 50 cm^3/min.

All chemicals were used of analytical or equivalent grade: 2-hydroxy benzaldehyde, semicarbazide, 4-phenyl 3-thiosemicarbazide, 4-4′-oxydianiline, N,N′-dimethyl *p*-phenylenediamine, hydrazine, formaldehyde and some organic solvents were purchased from E. Merck/Germany.

Synthesis. ***Formation of thiol schiff base.*** Some newer thiol schiff bases would be synthesized in the following sequence as:

Synthesis of bis[(2-hydroxy benzalthioyl) semicarbazone] (BHBSSc). Semicarbazide (2 mmol) was diluted in DMAc (10 mL) and added sulphur dust (160 mg). When the whole solution becomes homogenous, the content gives green colour, which show the positive response of diamines toward the sulphide ions. Added the mixture of (2 mmol) 2-hydroxy benzaldehyde in (10 mL) dimethyl acetamide. Refluxed the content by 118 ºC for 20 h with continual shaking in nitrogen environment. After heating, the content was poured in methanol (100 mL). The precipitates were filtered, re-crystallized in methanol (20 mL) and dried as pure product. (M.P ≥ 260 °C). The structural formula is also given in (Fig. 1).

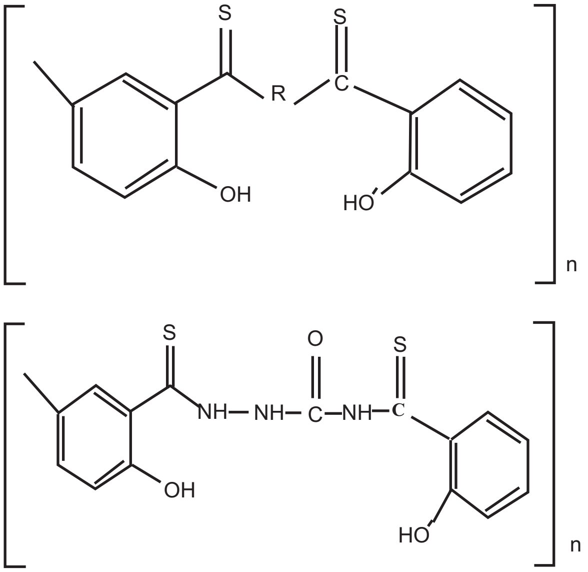

Fig. 1. Structural formula of poly[5-5′-methylene bis (2-hydroxybenzaldehyde) semicarbazone] (PMBHBSc)n.

Similarly, another diamines(4, phenyl 3-thiosemicarbazide), 4-4′-oxydianiline and N,N′-dimethyl *p*-phenylenediamine were also used instead to semicarbazide, for the syntheses of different polythiols like bis[(2-hydroxy benzalthioyl) 4-phenyl 3-thiosemicarbazone] (BHBPhTSc), bis[(2-hydroxl benzalthioyl) 4-4′-oxydianiline] ($BHBO_2A$)n and bis[(2-hydroxy benzalthioyl) N,N′-dimethyl *p*-phenylenediimine] ($BHBMe_2Ph$), respectively.

Formation of polythiol schiff base. ***Synthesis of poly5,5- methylene bis[(2-hydroxy benzalthioyl) semicarbazone] (PBHBSSc)n.*** The thiol schiff bases (TSB) would be dissolved in DMSO (50 mL) was added formaldehyde (0.01 M) with acetic acid (2 mL). The mixture was heated for 2 h at 120 °C.The precipitates were seperated and dried at 100 °C.The polythiols schiff bases formed having low melting points (M.P) than corresponding polyamides.

Results and Discussion

The composition and purity of newly synthesized schiff base polythiols (PMBHBSSc)n, (PMBHBSTSc)n, ($PMBHBO_2A$)n and ($PMBHBMe_2Ph$)n were confirmed by C.H.N elemental micro-analysis. After the confirmation of results, these polythiols were characterized by (FT-IR, UV/Vis) spectroscopic techniques. Then, the thermo-gravimetric and differential thermal analysis of these polythiols schiff bases were also recorded. The thermodynamic studies were also calculated by the means of intrinsic/absolute viscosity. These polythiols were soluble in highly polar solvents like THF, DMF and DMSO.

Characterization of polythiols. The FT-IR spectra of the polythiols(PMBHBSSc)n, (PMBHBSTSc)n, (PMBHBO$_2$A)n and (PMBHBMe$_2$Ph)n indicated the main characterized peaks C=C stretching vibration within1560-1660 cm^{-1} and C=S absorptions appeared within 1260- 1272cm^{-1}, (Fig 2a-b). Maximum sharp peaks obtained in the finger print region. The aliphatic C-H stretching for methylene generated by formaldehyde condensation about at 2810- 2906 cm^{-1} as a weak band, in these four polythiols.

The structure of newly synthesized compounds by various band frequencies of n- π^* and π-π^* transitions, due to the various unsaturated bonding like C=C, C=S, and C=O bonding. The measurements of UV/Vis spectra were accepted in THF solvent. Both schiff baseof the polythiols (PMBHBSSc)n, (PMBHBSTSc)n, (PMBHBO$_2$A)n and (PMBHBMe$_2$Ph)n indicate three absorption bands at 255-265 nm(1% ε =429.9-445.4 L/g/cm), 311- 318 nm (1% ε =245.6- 368.4 L/g/cm) and 385-48 nm (1% ε =251.3- 272.5 L/ g/cm. The initial band of polythiols showed the presence of unsaturated aromatic banding of compound, while last band appeared because of the formation of thiol bands of polythiols (Fig 3a-b).The last band is also responsible for the complete synthetic process of Willgerodt-Kindler reaction.

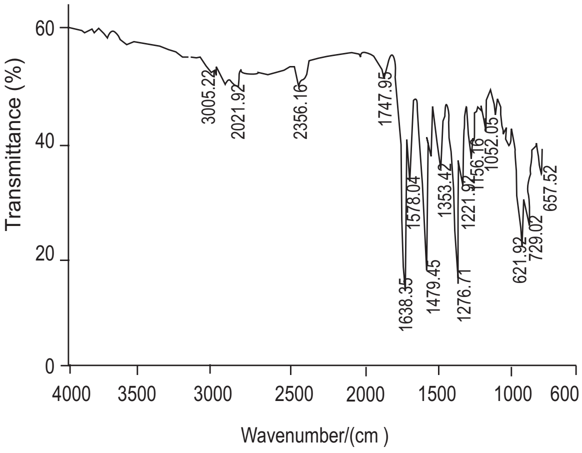

Fig. 2a. FT-IR spectrum of poly [5. 5′-methylene bis (2-hydroxy benzalthioyl) semicarbazone] (PMBHBSc)n.

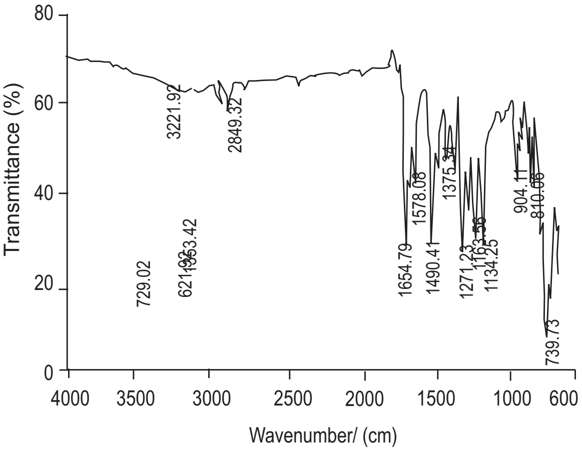

Fig. 2b. FT-IR spectrum of Poly [5. 5′-methylene bis (2-hydroxy benzalthioyl) N,N'-dimethyl p-phenylenediamine] (PMBHBMe$_2$Ph)n.

Thermal analysis (TG, DTA) techniques can be developed into quick life time prediction methods for polymers and provided a broad knowledge of the characterization of compounds. Measurement of dynamic relationship is based on two main factors, one is temperature and other is physical properties of the compound such as mass, volume or heat of reaction. The thermal gravimetric analysis of all polythiols is given in (Table. 1). According to the results, all newly

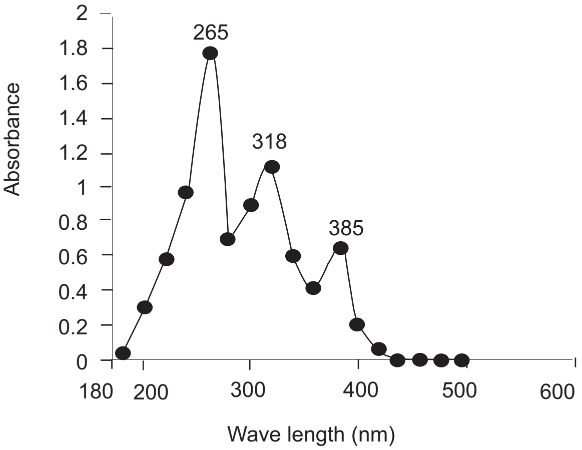

Fig. 3a. UV-vis spectrum of Poly [5. 5′-methylene bis (2-hydroxy benzalthioyl) semicarbazone] (PMBHBSc)n.

Table 1. Thermogravimetric data of some derived polythiols compounds at different temperatures

Characterization	(PMBHBSc)n	(PMBHBTSc)n	(PMBHBO$_2$A)n	(PMBHBMe$_2$Ph)n
Primary wt. loss	40 %	8 %	12 %	8 %
Temperature (°C)	220-490	250-280	260-310	280-310
Secondary wt. loss	26 %	52 %	55 %	22 %
Temperature (°C)	490-580	280-450	310-490	310-460
Tertiary wt. loss	34 %	42 %	29 %	68 %
Temperature (°C)	580-600	450-600	490-600	460-600
Total wt. loss	84 %	90 %	80 %	98 %

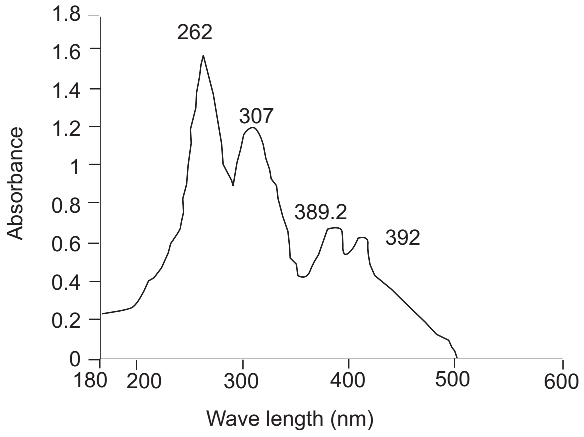

Fig. 3b. UV-vis spectrum of poly [5. 5′-methylene bis[(2-hydroxl benzalthioyl)) 4-4′-oxydianiline] (PMBHBO$_2$A)n.

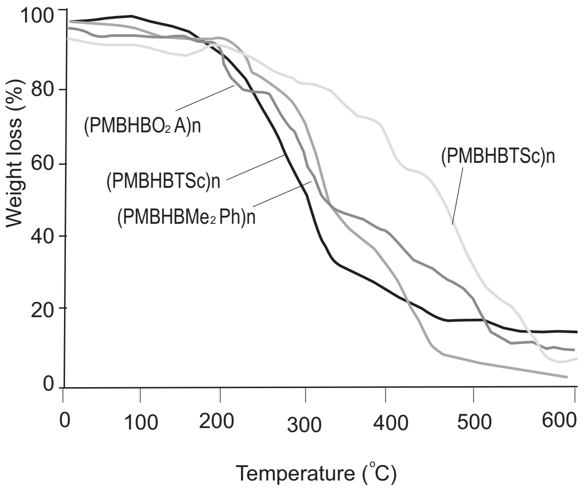

Fig. 4. Thermo-gravimetric analysis of some polythiols derived from bis (2-hydroxybenzaldehyde).

synthesized polythiols are thermal stable schiff base (Fig. 4). Thermal analyses were obtained from normal temperature to 600 ºC in N_2 environment atmosphere between room temperature and 600 ºC. The weight loss of polythiols started within 150-300 ºC and 80% to 90% weight loss followed but (PMBHBO$_2$A)n gave maximum stability due to the aromatic bulky rings.

The viscosity measurements of these polythiols were noted with different concentrations and temperatures. Various viscosities were measured with these polythiols. The graph reduced viscosity (η red) v/s different concentrations, gave a linear curve which indicated that increase in reduced viscosity is directly proportional to concentration, whereas inversely proportional to temperature. Intrinsic viscosity (η) of the polythioamides (PMBHBSSc)n, (PMBHBSTSc)n, (PMBHBO$_2$A)n and (PMBHBMe$_2$Ph)n were measured in 0.393-0.473 dL/g to 0.437-0.509 dL/g. The values of ΔG_v were also calculated by means of their absolute viscosity of these schiff base polythiols (PMBHBSSc)n 12.28-14.615 and (PMBHBSSc)n 13.126- 14.63 kJ/mol. The change in enthalpy relation with concentration that's why enough energy is required for smooth flow of bulky polythiols.

Conclusion

The work reports the synthesis of four new polythiols by Willgerodt Kindller method. As these polythiols were formed by the induction of sulfur element so new bonds would be shown as thio group, after reaction. Therefore, spectroscopic characterizations (FT-IR and UV-Vis) also carried out with these polythiols. Somew hat improvement was also achieved in TG/ DTA analysis in polythiolsas compared to their polyamides. The polythiol (PMBHBMe$_2$Ph)n has about 98 % total weight loss at 600 °C, while polythiol (PMBHBO$_2$A)n has 80% total weight loss at same temperature. The viscometry data also recorded and gave valuable information for their structural composition.

As sulphur-based polymers (polythiols) are natural, eco-friendly, bio-compatible and bio-degradable biological active and have a low health hazard due to the similar properties of imines-based schiff bases polymer. Therefore, further applicable studies will be obtained in future.

Conflict of Interest. The authors declare they have no conflict of interest.

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