# Thermoanalytical Studies of Some Schiff Base Polymers and Their Metal Chelates

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**Summary**: Thermogravimetry (TG) and differential thermal analysis (DTA) of poly 5,5'-methylene-bis-salicylaldehyde-tetramethylenediimine (PMSATen), poly 5,5'-methylene-bis-salicylaldehyde-meso-stilbenediimine (meso-PMSAS), poly 5, 5'-methylene-bis-salicylaldehyde-dl-stilbenediimine (dl-PMSAS), poly 5,5'-methylene-bis-salicylaldehyde-2,6-diiminopyridine (PMSAP), and their copper (II) and nickel (II) chelates were recorded in nitrogen atmosphere upto 800 °C. Loss in weight occurs in two to three stages. The polymers and their nickel chelates indicate better thermal stability as compared to their corresponding copper complexes. DTA shows a series of endotherms with maximum in the range of 400-700 °C.

## Introduction

TG and DTA are widely used to investigate thermal decomposition of polymers [1-7]. The thermal stability of aromatic polymeric Schiff bases is reported to be comparable to aromatic polyamide [4]. The variation in thermal decomposition of Schiff base polymers with their structures and complexation with metal ions have been reported [4, 8, 9]. Recently, preparation and characterization of Schiff base polymers PMSATen, meso-PMSAS, dl-PMSAS, PMSAP and their copper and nickel complexes have been reported [10] (Fig. 1) and the present work examines the thermoanalytical behavior of these compounds in nitrogen atmosphere, to evaluate their thermal stability for their possible use as high temperature polymers.

## Results and Discussion

TG of the polymers PMSATen, meso-PMSAS and dl-PMSAS indicate weight loss in three stages, initial loss of upto 12 % in temperature range of 160-330 °C, and an additional secondary loss of 15-20 % upto the temperature in range of 380-600 °C. This is followed by a rapid total loss of 95-100 % upto temperature 720-800 °C. TG of PMSAP indicates slightly different pattern with loss in weight in two stages. Loss of 4 % in temperature range 190-340 °C, followed by rapid loss upto 96 % by 590 °C. The initial loss of upto 12 % may be attributed to the absorbed solvent present in the polymers followed by thermal decomposition in one to two stages upto 800

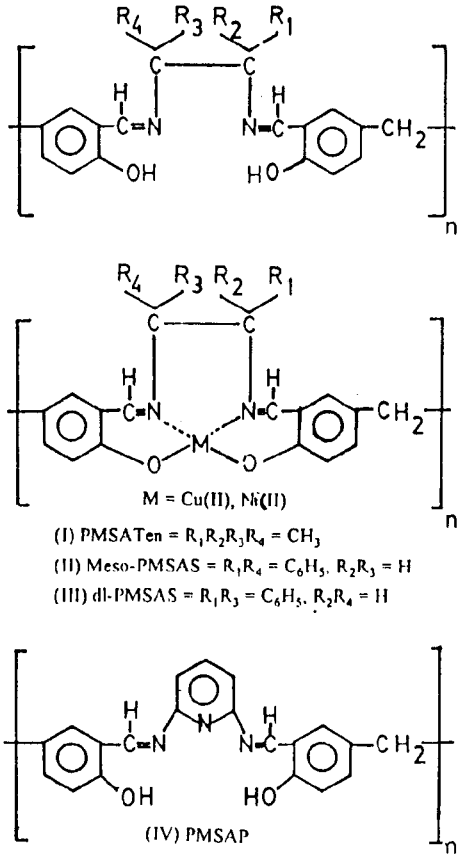


Fig. 1. Structural diagram of Schiff base polymers and their polymetal chelates.

Table 1. Thermal analysis of polymers and their copper (II) and nickel (II) polychelates

| Polymer | Copper (II) Polychelate | Nickel (II) Polychelate |
|---|---|---|
| 1 Loss in weight in dl-PMSAS started at 230 °C and loss of 10 % by 25 °C and an additional secondary loss of 15 % within 400-600 °C. This was followed by rapid and total loss of 95 % upto 800 °C. DTA showed three endotherms at 190 °C, may be due to loss of solvent, second endotherm at 660 °C and a large decomposition endotherm at 740 °C. | Loss in weight started at 110 °C and loss of 7 % by 280 °C, followed by secondary loss of 12 % within 350-400 °C and total loss of 80 % by 670 °C, with maximum rate of loss at 540 °C. DTA shows three endotherms at 300 °C, 330 °C and a large decomposition at 530 °C. | Loss in weight started at 220 °C and loss of 10 % by 295 °C, followed by secondary loss of 14 % within 400-540 °C. Total loss of 93 % observed upto 800 °C with rapid rate of loss at 600 °C. DTA showed endotherms at 280 °C, 650 °C and largest at 770 °C. |
| 2 TG of meso-PMSAS indicated that loss in weight was started at 230 °C with loss of 10 % by 290 °C, followed by secondary loss of 20 % within 480-550 °C. Total loss of 100 % was observed at 680 °C with maximum rate at 600 °C. DTA showed endotherms at 180 °C, 260 °C and the largest decomposition at 660 °C. | Loss is weight started at 110 °C and loss of 7 % by 300 °C, followed by a final loss of 69 % upto 500 °C, with maximum rate at 420 °C. DTA showed endotherm at 270 °C and larger at 400 °C. | Loss in weight started at 120 °C and loss of 3 % by 310 °C, followed by a loss of 82.5 % by 590 °C with maximum rate at 460 °C. DTA showed endotherm at 130 °C and larger at 650 °C. |
| 3 Loss in weight in PMSATen started at 160 °C and loss of 12 % by 275 °C, followed by loss of 17 % within 280-410 °C and total loss of 98 % by 720 °C with maximum rate at 550 °C. DTA shows endotherms at 150 °C and larger decomposition at 595 °C. | Loss in weight started at 110 °C and loss of 6 % by 300 °C and secondary loss of 67 % upto 500 °C, with maximum rate at 380 °C. DTA showed endotherms at 290 °C and a largest at 420 °C. | Loss in weight started at 120 °C and loss of 5 % by 320 °C, followed by total loss of 81 % by 650 °C with maximum rate of loss at 520 °C. DTA showed endotherms at 405 °C, 530 °C and large endotherm at 630 °C. |
| 4 Loss in weight started at 190 °C and loss of 4 % by 340 °C, followed by 690 °C, with maximum rate of loss at 590 °C. DTA showed two endotherms at 360 °C and large decomposition at 600 °C. | | |

°C. The loss of weight of PMSAP by 590 °C may be attributed to lower molecular weight of the polymer as compared to dl-PMSAS, meso-PMSAS and dl-PMSAS [10]. The phenyl substituted dl-PMSAS and meso-PMSAS have higher thermal stability as could be expected due to the phenyl groups substitution at bridge position (Table 1). DTA of PMSATen, meso-PMSAS, dl-PMSAS, PMSAP indicate small endotherms due to the loss of solvent and characteristic large endotherms within 595-660 °C due to vaporization/ decomposition. PMSAP also shows prominent endotherm at 360 °C (Fig. 2) may be due to melting.

The copper (II) and nickel (II) chelates of PMSATen, meso-PMSAS and dl-PMSAS also lose weight in two to three stages in the range of 70-94 % upto 800 °C. Each of the compound left dark residue, contributed mostly by metallic compounds. They were cleaned from platinum crucible by hydrochloric acid (1 N). The loss in weight in nickel chelates occur 3-10 % upto 320 °C and total loss of 81-93 % upto 800 °C. Copper (II) polychelates show 6-7 % loss upto 300 °C and 67-69 % loss upto 670 °C. The loss in weight in nickel (II) polychelates occurs at higher temperature than corresponding copper (II) polychelates. Thus more planar nickel polychelates indicate higher thermal stability than corresponding copper (II) polychelates (Table 1). DTA of copper (II) polychelates indicate two to three endotherms within 270-530 °C. The first may be due to the melting transition, followed by decomposition endotherm (Fig. 3a). Similarly nickel (II) chelates also indicate two to three prominent endotherms in the temperature range of 130-770 °C (Fig. 3b), due to loss of solvent, melting and decomposition endotherms.

In order to examine the effect of metal chelation on thermal stability of Schiff base polymers, TG of dl-PMSA, dl-PMSASNi and dl-PMSASCu recorded under similar conditions were

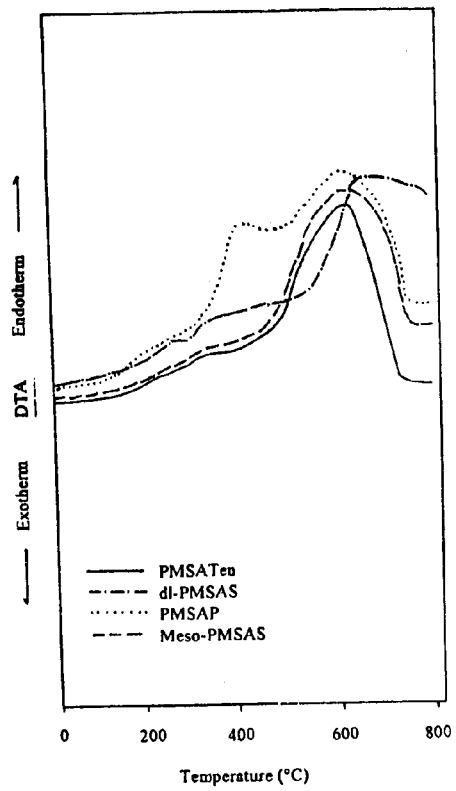


Fig. 2. DTA of Schiff base polymers at a heating rate of 15 °C/ min, with nitrogen flow rate of 50 cm3/ min.

compared. It was observed that dl-PMSAS indicated weight loss at higher temperature than the corresponding nickel and copper chelates (Fig. 4). Thus it may be concluded that the chelation with copper (II) and nickel (II) of Schiff base polymers examined in the present work did not improve the thermal stability of the polymers.

## Experimental

The Schiff base polymers PMSATen, meso-PMSAS, dl-PMSAP and their copper and nickel complexes were prepared as reported [10]. Thermogravimetry (TG) and differential thermal analysis (DTA) of the compounds were carried on Shimadzu DT-30 B thermal analyzer from room temperature to 800 °C with a heating rate of 15 °C/ min and nitrogen flow rate of 50 $cm^3$/ min. The sample of 10 ± 0.5 mg was used in platinum crucible and was recorded against α-alumina as reference.

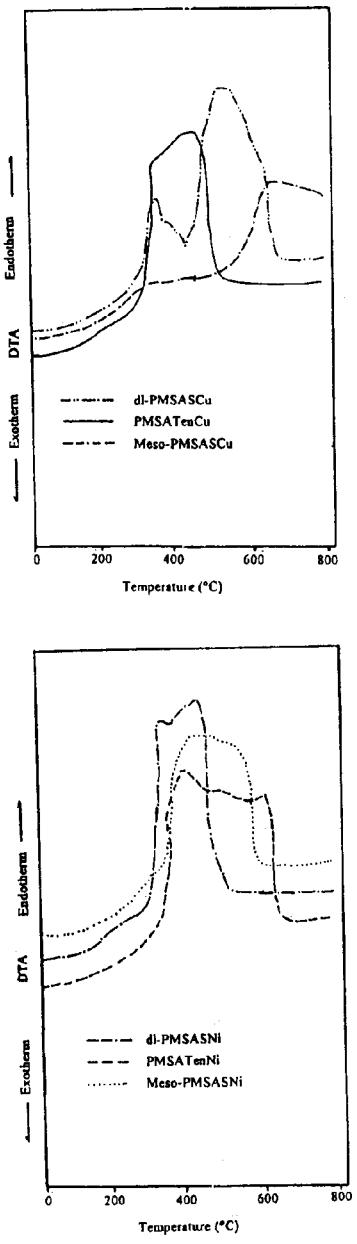


Fig. 3. DTA of (a) poly copper (II) chelates (b) poly nickel (II) chelates. Conditions as in Fig. 2.

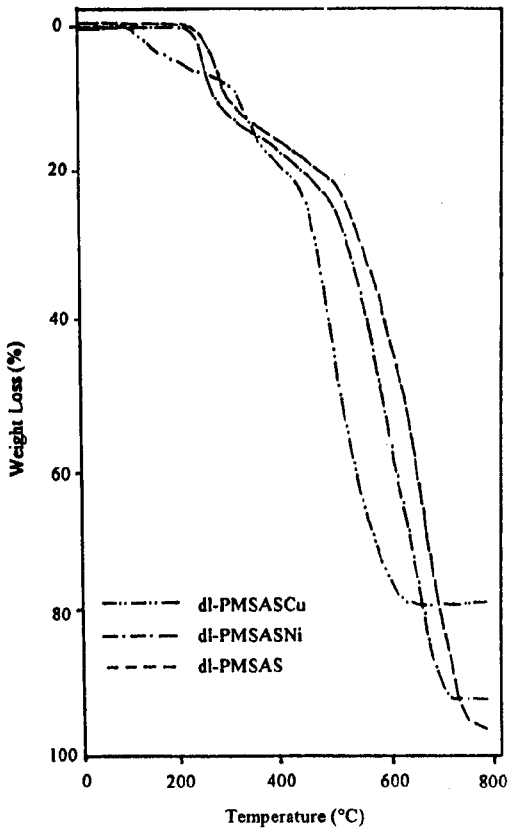


Fig. 4. Comparative TG of dl-PMSAS and its copper and nickel chelates. Conditions as in Fig. 2.

## Conclusion

TG and DTA of four polymers and six polychelates have been examined in nitrogen atmosphere. Phenyl groups substitution have a positive effect on thermal stability of polymers. The Schiff base polymers and their copper and nickel polychelates indicate main decomposition loss in temperature above 300 °C.

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