*Sindh Univ. Res. Jour. (Sci. Ser.) Vol.46 (1): 37-40 (2014)*

**SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)**

# Synthesis and Characterization of Newly Schiff Base Polymers of 4, 4'- Methylene Bis (Cinnamaldehyde) With Urea and 1,2-Phenylenediamine

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Received 28th December 2013 and Revised 10th February 2014

**Abstract:** Dialdehyde Methylene Bis (Cinnamaldehyde) (MBC) and Schiff base polymers was synthesized by polycondensation reaction with urea and 1,2-phenylenediamine in acidic media and was characterized by C. H. N elemental analysis, UV/Vis spectroscopic techniques, thermal analysis and viscosity measurements. The synthesized Schiff base polymers indicated better thermal stability up to 700ºC than dialdehyde (MBC). The dialdehyde (MBC) and its derived polymers were soluble in tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethyl sulphoxide (DMSO). The intrinsic viscosities ranged within 0.276-0.316 dL/g for (PMBCUR) and 0.264- 0.324 dL/g for (PMBCPh) as compared to 0.174-0.249 dL/g for dialdehyde in THF.

**Keywords:** Synthesis, Schiff base polymers, Infrared spectroscopy, U/V-visible spectroscopy, Thermal analysis.

## 1. INTRODUCTION

A wide variety of structurally related Schiff base polymers has been synthesized. They have attracted main attention in research due to their significance in many aspects.

Some of the Schiff bases are prepared from aromatic dialdehyde compounds with different diamines and they exhibited unusually good resistance to decomposition by heat (Aly, *et. al.* 2000); (Catanescu, *et. al.* 2001) and (Grigoras, *et. al.* 2001). The comparative thermal stabilities of the products in air and nitrogen atmosphere were investigated by thermogravimetric analysis (Lux. O, 2003); (Lacroix,, *et. al.* 2001). The influence of chemical structure on thermal stability was shown and the factors that might provide a lead for making high-molecular-weight polymers with better heat resistance were also discussed (Khuhawar, *et. al.* 2004).

Phenylenediamine has been used as diamines in the synthesis of two isomeric Schiff base polymers by polymerization reaction of two different monomers, N,N-dibenzylidene-p-phenylenediamine, N,N-dibenzylidene-m-phenylenediamine (Alelio, *et. al.* 1967).

All the polyazomethines were amorphous and most of them were highly soluble in various organic solvents, especially in tetrahydrofuran (THF), dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO). Thermal analysis were indicating that these Schiff base polymers had high $T_g$ and excellent thermal stability (Gutch, *et. al.* 2001); (Cazacu,, *et. al.* 2003). The characterization by viscometric measurements involved the determination of various important parameters of a polymer like structure, molecular size and shape, which give the information about the macromolecules (Marcia, *et. al.* 2005). The difference is obtained due to the difference in the size of solvents and solute (*Ivana, et.al. 2006)*. Some of the Schiff bases of cinnamaldehyde has been successively synthesized using different diamines such as ethylenediamine, 1,2- propylenediamine, 1,3-propylenediamine, semicarbazide and thiosemicarbazide (Shah, *et al.* 2007).

The present work examines the synthesis of two new Schiff base polymers of methylene bis cinnamaldehyde by polycondensation of urea and 1,2-diaminobenzene in acidic media. Polymeric products were obtained in moderate to good yields and their confirmation supported by spectroscopic, thermogravimetric and viscosities measurements.

## 2. MATERIAL AND METHODS

### Materials

Cinnamaldehyde, urea, 1,2-diaminobenzene (E. Merck, Germany), glacial acetic acid, chloroform, *n*-hexane, dimethyl acetamide (DMAc), methanol, dimethyl formamide (DMF) and tetrahydrofuran (THF) (Fluka, Switerzerland) were used.

### Apparatus

The elemental micro-analyses were carried out by an elemental Micro Analysis Devon (UK). Infrared

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spectra of compounds were recorded on the Perkin Elmer 1430 IR spectrophotometer using KBr pellet techniques in the range of 4000-200 $cm^{-1}$. Instrument was also calibrated by polystyrene film for the accuracy of results. Spectrophotometric studies were carried out in dimethyl formamide (DMF) and tetrahydro furan (THF) on a double beam Hitachi 220 spectrophotometer (Hitachi 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 500ºC with a nitrogen flow rate of 50 mL/min. Sample (10 mg) was placed in platinum crucible and its weight was recorded against alumina as a reference at a heating rate of 10ºC/min. The proton nuclear magnetic resonance $^1$H NMR spectra of dialdehyde and their polymers were recorded on a Bruker ACF 300 spectrometer, using dimethylsulphoxide (DMSO) as a solvent and tetramethyl silane (TMS) as an internal reference. The viscosity measurements of dialdehyde (MBC) and their derived polymers 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.

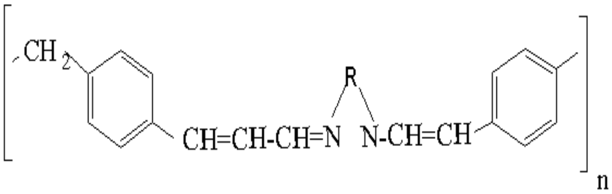
## SYNTHESIS OF DIALDEHYDE 4, 4'-METHYLENE BIS(CINNAMALDEHYDE):

The dialdehyde of [4,4'-methylene bis(cinnamaldehyde)] was prepared and purified by procedure as reported earlier.

## SYNTHESIS OF SCHIFF BASES POLYMERS FROM 4,4'-METHYLENE BIS (CINNAMALDEHYDE):

4, 4'-methylene bis(cinnamaldehyde) (MBC) (2.76 g) dissolved in THF (60 mL) and acetic acid (10 mL) was added urea (0.6 g) or 1,2–diaminobenzene (1.68 g) dissolved in THF (3 mL ) and acetic acid (5 mL). The contents were refluxed for 24 hours and half of the solvent was distilled off. The remaining solution was diluted with methanol (50 mL). The precipitate obtained was filtered and recrystallized from the mixture of chloroform/n-hexane and dried in oven for 8 h at 110 $^{o}$C till free floating compound was obtained. All compounds were decomposed at 340- 360 $^{o}$C. The chemical structures of MBC and its Schiff base polymers are shown in **(Fig: 1).**

**(1)** Poly[4,4'-methylene(bis cinnamaldehyde)urea] (PMBCUR)



R = PMBCUR = CO
R = PMBCPh = o–$C_6H_4$

**Fig: 1: Structure diagrams of Schiff base polymer 4- 4'-methylene (biscinnamaldehyde) with different diamines.**

IR: 3053, 3028, 2938, 2870, 1720, 1623, 1602, 1220, 1150, 1074, 1060, 790, 710 $cm^{-1}$.
Analysis of $(C_{20}H_{16}N_2O)n$, calculated: C, 80.0 %; H, 5.34 %; N, 9.33 %.
Found: C, 79.88 %; H, 5.26 %; N, 9.15 %.

**(2)** Poly[4,4'-methylene(bis cinnamaldehyde)1,2-phenylenediimine] (PMBCPh)
IR: 3072, 3018, 2940, 1635, 1595, 1500, 1216, 1112, 1044, 1026, 787, 742 cm-1.
Analysis of $(C_{25}H_{20}N_2O)n$, calculated: C, 86.21 %; H, 5.74 %; N, 8.04 %.
Found: C, 85.68 %; H, 5.56 %; N, 7.89 %.

## 3. RESULTS AND DISCUSSION

The results of elemental micro-analysis agreed closely to the expected values. The prepared dialdehyde was used to synthesize newer Schiff base polymers by polycondensation with urea and 1,2-Phenylenediamine. Polycondensation reactions were carried out by the addition of acetic acid. Its reproducible results were obtained between theoretical and found values, by elemental analysis of polymers. The solubility of MBC and its Schiff base polymers were examined in different organic solvents such as acetone, butanol and chloroform THF, DMF, DMSO but these compounds were completely soluble in THF, DMF and dimethyl sulphoxide (DMSO)**.** Therefore the solvents with high dielectric constant are preferred as the solvent system for the polymers.

The dialdehyde MBC and polymers were characterized by IR spectroscopic techniques. There was a main difference between IR spectra of the dialdehyde and Schiff base polymers. IR spectrum of the MBC gave strong bands at 1730 and 1700 $cm^{-1}$ due to υC=O vibrations. The corresponding bands in spectra of the polymer (PMBCPh) were either absent or observed only as weak bands due to polycondensation **(Fig. 2).** The polymers PMBCUR indicated strong bands at 1672 $cm^{-1}$ due to the presence of υC=O groups, contributed by urea. Both Schiff base polymers indicate a characterized band within 1660−1620 $cm^{-1}$ due to υC=N vibrations. The dialdehyde MBC and its polymers indicated two to three bands within 1590−1480$cm^{-1}$duetoaromaticringand υC=C vibration.

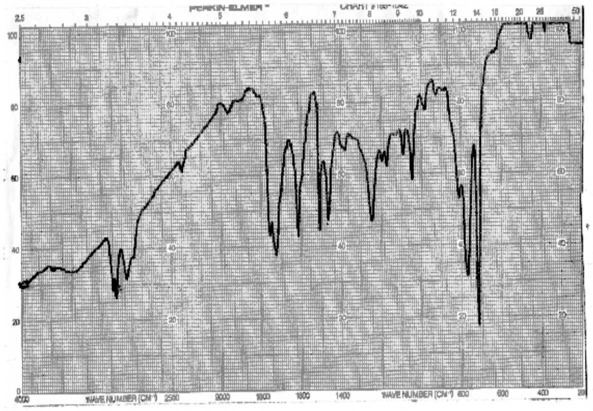


**Fig: 2: Infrared Spectrum for dialdehyde of (MBC)**

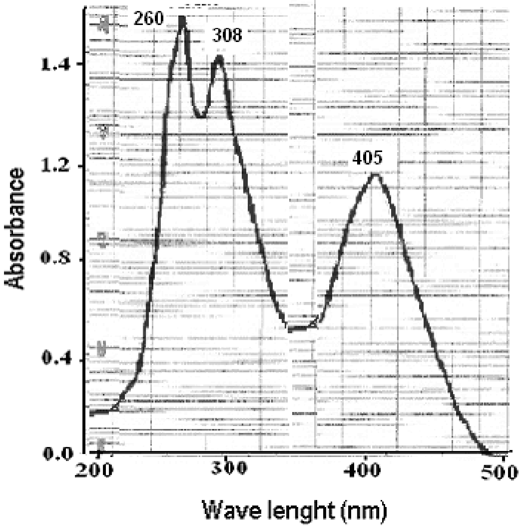


**Fig: 3: U/V-Vis Spectrum for Schiff base polymer of (PMBCPh).**

The measurements of UV/Vis spectra were carried out in THF and DMF. The dialdehyde MBC indicates two absorption bands at 262 and 338 nm with the molar absorptivity of 2.3 × $10^4$ and 1.0 × $10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$ due to π- π* transition in the benzoid rings and π- π* conjugated carbonyl groups respectively. The polymers indicate three bands **(Fig. 3),** and the observation of a new band or the shift in the position of the band as compared to MBC may be attributed to conjugated azomethine chromophores incorporated in the polymers due to polycondensation. Thermoanalytical studies were carried out in nitrogen atmosphere from room temperature to 800 ºC. The weight loss in the case of MBC started at 220ºC and 100% loss was observed at 620ºC, but in both Schiff base polymers (PMBCUR and PMBCPh) weight loss started within 262−700ºC and 80-88% weight loss occurred up to 700ºC. The **(Fig. 4),** indicates an improvement in thermal stability of polymers due to polymerizations.

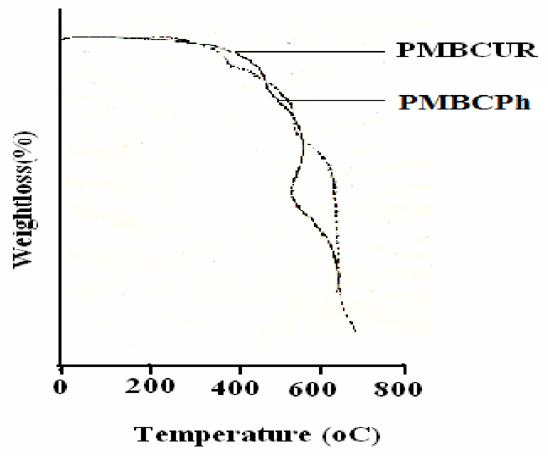


**Fig. 4: TGA curves of Schiff base polymers of (biscinnamaldehyde) obtained at a heating rate 10 K/min and nitrogen flow rate of 50 mL/min.**

The viscosity measurements of synthesized dialdehyde MBC and the Schiff base polymers 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 polymers (PMBCUR) and (PMBCPh) were in the ranges of 0.276−0.316 and 0.264−0.324 dL/g, respectively. The relationship between the reduced viscosity and concentration in the range of 0.02 to 0.08 g/dL was linear for both the compounds, and an increase in reduced viscosity was observed by increase in the concentration and decrease in the temperature **(Fig. 5).** Both the polymers indicated higher values of intrinsic viscosity than that of dialdehyde MBC and these results also support the formation of the polymers. Absolute viscosity increased with concentration due to the increase in density of solutions **(Table: 1)** and possible formation of associates. A decrease in $\eta_{abs}$ by increase in temperature can be attributed to the increase

**Absolute viscosity of Schiff base polymer (PMBCPh) ($m.N.S/m^2$)**

| 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 |

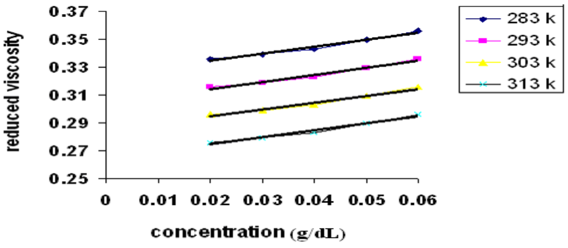


**Fig 5: Reduced viscosity v/s concentration of Schiff base polymer (PMBCPh).**

in volume and decrease in density. A decrease in associations among polymer molecules can also occur at higher temperatures. All thermodynamic parameters of dilute solutions of dialdehyde and polymers were calculated in THF. The values of $\Delta G$v for MBC were 12.0−14.1 kJ mol$^{-1}$ as compared to the polymers PMBCUR 13.11−14.6 kJ mol$^{-1}$ and PMBCPh14.27-14.59 kJ mol$^{-1}$. The value of $\Delta G$v for dialdehyde and their polymers increased with increase in temperature as well as the concentration. An increase in $\Delta G$v with increase in temperature indicates that shape transition of the polymer molecules takes place during flow process. The values of $\Delta H$v for dialdehyde were 11.5−11.7 kJ mol$^{-1}$ higher than those of the polymers PMBCUR (7.95−8.11 kJ mol$^{-1}$) and PMBCPh (6.85−7.02 kJ mol$^{-1}$). The values of $\Delta H$v increased by increase in the concentration because more energy was required to overcome the force of attraction among the molecules themselves during their flow. However the values of $\Delta H$v of viscous flow are less dependent on temperature, may be the polymers are less crosslinked in THF. A lower value of $\Delta H$v was observed in polymers as compared to that of dialdehyde (MBC), possibly, because of the aggregation of polymer molecules. The values of $\Delta S$v of MBC were from −0.0013 to −0.0081 J/K, while those of the polymer PMBCUR were in the range of −0.0112 to −0.0197 J/K. The negative sign of $\Delta S$v for polymers shows that during flow the molecules are becoming more extended due to the uncoiling of the polymer molecules in the solution.

## 4. CONCLUSIONS

The work reported the synthesis of dialdehyde and two Schiff bases polymers by simple synthetic routine. The formation of the polymers was confirmed by characterization of the polymers by elemental microanalysis, IR, UV/Vis spectroscopy, thermogravimetric analysis and viscosities measurements. Some improvements in thermal stability were also observed in polymers. The polymers indicated solubility in common solvents including chloroform and acetone.

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