Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Khuhawar, M. Y. and Channar, A. H.(1995) 'Syntheses and Characterization of New Schiff Base Polymers and Their Copper(II) and Nickel(II) Chelates', Journal of Macromolecular Science, Part A, 32: 2, 523 — 530

To link to this Article: DOI: 10.1080/10601329508019197

URL: http://dx.doi.org/10.1080/10601329508019197

MACROMOLECULAR REPORTS, A32(SUPPL. 4), 523-530 (1995)

SYNTHESES AND CHARACTERIZATION OF NEW SCHIFF BASE POLYMERS AND THEIR COPPER(II) AND NICKEL(II) CHELATES

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ABSTRACT

Four new Schiff base polyemrs poly 5,5'-methylenebis-salicylaldehyde-tetramethylethylenediimine(PMSATen), poly5,5'-methylenebis-salicylaldehyde-meso-stilbenediimine(meso-PMSAS), poly5,5'-methylenebis-salicylaldehyde-dl-stilbenediimine(dl-PMSAS) and poly5,5'-methylenebis-salicylaldehyde 2,6-diiminopyridine(PMSAP) and their copper(II) and nickel(II) chelates have been synthesized. They have been characterized by elemental micro-analysis, intra red and ultraviolet/visible spectrophotometry. The reduced viscosity of PMSATen, meso-PMSAS and dl-PMSAS measured in tetrahydrofuran (THF) was found in the range of 0.135-0.315.

INTRODUCTION

A number of Schiff base polymers have been reported [1-5] by polycondensation of terephthaldehyde [6,7] glyoxal [7], bissalicylaldehyde-5,5'-sulfone [2,8], 5,5'-methylenebis-salicylaldehyde [1,5,8,11], 4,4'-dihydroxy-3,3'-diacetylbiphenyl [12] and 3,3'-diamino-4,4'-diformyldiphenylsulfone [13] with different diamines. They have attracted attention as solid phase in gas chromatography [14] and as catenation ligands, where they have been studied as coordination polymers [11,12]. Thermal stability of Schiff base polymers is also reported as comparable to polyamides [5, 7-8]. In the present work some new polymeric Schiff bases and their copper(II) and nickel(II) chelates have been prepared and characterized.

EXPERIMENTAL

Preparation of Poly-5,5'-methylenebis(salicyl-aldehyde)meso-stilbenediimine(mesoPMSA-S) and poly-5,5 -methylenebis(salicyl-aldehyde)dl-stilbenediimine-(dl-PMSAS).

To the solution of 5,5 -methylenebis-salicylaldehyde (0.521 g) in tetrahydrofurn (THF) (3 ml) and acetic acid glacial (10 ml) was added meso-stilbenediamine (0.22 g) or dl-stilbenediamine (0.22 g) dissolved in THF (5 ml) and acetic acid (5 ml). The mixture was refluxed for 2 hrs. The mixture was diluted with ethanol (50 ml). The precipitate obtained was filtered and washed with water, ethanol and diethyl ether. Precipitate was recrystallized from tetrahydrofurn-ethanol (1:1).

Preparation of Poly-5,5'-methylenebis(salicylaldehyde)-tetramethylethylenediimine(PMSATen)

To a solution of 5,5'-methylenebis-salicylaldehyde (0.52 g) in THF (5 ml) and acetic acid (10 ml) was added tetramethylethylenediamine in diethyl ether (0 ml). The mixture was refluxed for 2 hrs and the volume of the solution was decreased to half. The remaining solution was diluted with ethanol (50 ml). Precipitate formed was filtered and washed with water, ethanol and diethyl ether. The product was recrystalizied from tetrahydrofurn: ethanol (1:1).

Preparation of Poly-5,5'-methylenebis(salicylaldehyde)-2,6-diiminopyridine(PMSAP)

5,5'-Methylenebis-salicylaldehyde (1.2 g) dissolved in THF (5 ml) and acetic acid glacial (10 ml) was added freshly recrystallized 2,6-diaminopyridine(0.22 g) dissolved in tetrahydrofurn (5 ml). The precipitate appeared quickly, but the mixture was heated on water bath for 30 min. The mixture was diluted with ethanol (50 ml). Precipitate was filtered and washed with water, ethanol, THF and diethyl ether.

Preparation of Copper(II) and Nickel(II) Chelates

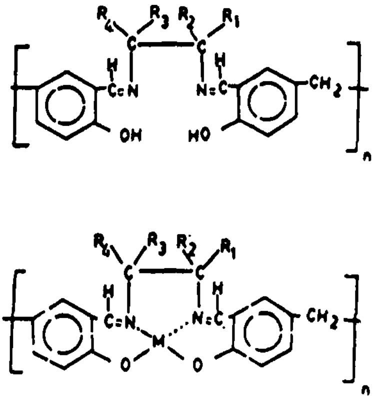
To the solution of PMSATen, meso-PMSAS or dl-PMSAS (0.5 g) in THF (20 ml) was added solution of nickel(II) acetate (0.5 g) or copper(II) acetate(0.4 g) dissolved in THF (20 ml). The mixture was added acetic acid (1 ml) and refluxed for 15 min. The mixture was allowed to cool at room temperature and was stirred continuously for 6 days. The precipitate was filtered and washed with water, ethanol THF and diethyl ether.

5,5 -Methylenebis-salicylaldehyde was prepared as reported by Marvel and Tarkoy [1]. Meso and dl-stilbenediamines(1,2-diamino-1,2-diphenylethane) were prepared as reported [15,16]. meso-Stilbenediamine was prepared from hydrobenzamide to amarine, N-benzoyl- N-acetyl-meso-stilbenediamine and meso-stilbenediamine [15]. dl-Stilbenediamine was prepared from hydrobenzamide to amarine, isoamarine, N-benzoyl-N-acetyl-dl-stilbenediamine and dl-stilbenediamine. Tetramethylethylenediamine(2,3-Diamino-2,3-dimethylbutane) was prepared by the reduction of 2,3-dimethyl-2,3-dinitrobutane with granular tin in hydrochloric acid using reported method [17]. 2,6-diaminopyridine (E. Merck) was recrystallized from n-hexane before use.

Elemental micro-analyses were carried out by HEJ-Research Institute of Chemistry, University of Karachi. Infra red spectra of the compounds in KBr were recorded on Perkin Elmer 1430 IR spectrophotometer within 4000-200 cm^{-1}. Spectrophotometric studies in THF and dimethyl sulfoxide (DMSO) were carried out on Hitachi 220 Spectrophotometer. The viscosities of meso-PMSAS, dl-PMSAS and PMSATen in THF (1 g in 100 ml solvent) were measured at 30°C ± 0.2°C using suspended level viscometer (Technico ASTMD 445). Gallenkamp viscometer bath VS615 was used to control the temperature. Reduced vasocity (η red) was calculated by dividing specific viscosity (nsp) with concentration (g/100 ml).

RESULTS AND DISCUSSION

In the present work four polymeric Schiff bases have been synthesized by the poly condensation of 5,5 -methylenebis-salicylaldehyde with different diamines. (Fig.1) The compounds were obtained in good yield (70-90% theoretical). Polymer PMSAP readily precipitated from the reaction mixture in THF, but reaction mixture was heated on water bath to complete the reaction. Polymers meso-PMSAS, dl-PMSAS and PMSATen are soluble in THF and acetic acid mixture, and the product was isolated after the addition of ethanol. Polymers PMSATen, meso-PMSAS and dl-PMSAS are soluble in THF, DMSO, ethyl acetate and N,N -dimethylformamide (DMF), but PMSAP is only slightly soluble in DMSO. The copper(II) and nickel(II) chelates of PMSATen, meso-PMSAS and dl-PMSAP were easily prepared, following general synthetic procedure, but difficulties were encountered in the preparation of copper(II) and

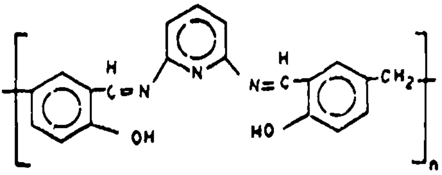


M = Cu(II), Ni(II)

(I) PMSATen: $R_1R_2R_3R_4 = CH_3$

(II) meso-PMSAS: $R_1R_4 = C_6H_5$, $R_2R_3 = H$

(III) dl-PMSAS: $R_1R_3 = C_6H_5$, $R_2R_4 = H$



(IV) PMSAP

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

nickel(II) chelates of PMSAP, because of its low solubility in most of the solvents. The metal chelates prepared were also slightly soluble in DMSO. The results of elemental micro analysis (Table 1) agree reasonably with the expected values.

The Schiff base polymers indicate a strong band around 1630 cm^{-1} corresponding to hydrogen bonded ν C=N and two bands at 1590-80 cm^{-1} and 1490 cm^{-1}due to νC=C vibrations. The compounds meso-PMSAS, dl-PMSAs and PMSAP indicate a week band around 1660-55 cm^{-1}, may be due to -C=O present as an end group. Comparing the relative intensity of the bands observed at 1630 cm^{-1}

TABLE - I

RESULTS OF ELEMENTAL MICRO ANALYSIS

NAME OF COMPOUND	CHEMICAL FORMULA	M.P. °C	YIELD THEORITICAL %	EXPECTED % FOUND %		
				C	H	N
1. meso-PMSAS	$(C_{29}H_{24}O_2N_2)n$	185	80	80.523	5.595	6.481
				80.194	5.605	5.734
2. dl-PMSAS	$(C_{29}H_{24}O_2N_2)n$	180	75	80.523	5.593	6.481
				79.455	5.576	5.479
3. PMSATen	$(C_{21}H_{24}O_2N_2)n$	220	70	74.961	7.193	8.331
				74.432	7.146	8.253
4. PMSAP	$(C_{22}H_{15}O_2N_3)n$	230	90	73.870	4.430	12.322
				73.521	4.523	12.183
5. meso-PMSASCu	$(C_{29}H_{22}O_2N_2Cu)n$	>350	85	70.50	4.49	5.67
				69.51	4.49	4.67
6. meso-PMSASNi	$(C_{29}H_{22}O_2N_2Ni)n$	>350	90	71.19	4.52	5.73
				71.20	4.52	5.73
7. dl-PMSASCu	$(C_{29}H_{22}O_2N_2Cu)n$	>350	89	70.50	4.49	5.67
				70.85	4.62	4.84
8. dl-PMSASNi	$(C_{29}H_{22}O_2N_2Ni)n$	>350	80	71.19	4.52	5.73
				70.85	4.62	4.84
9. PMSATenCu	$(C_{21}H_{22}O_2N_2Cu)n$	>300	90	63.37	5.57	7.04
				63.12	5.23	7.15
10 PMSATenNi	$(C_{21}H_{22}O_2N_2Ni)n$	>300	89	64.15	5.65	7.13
				64.50	5.85	6.50

and 1660 cm^{-1}, it is observed that weakest band at 1660 cm^{-1} is observed in PMSATen followed by in sequence, with increasing relative intensity in dl-PMSAS, meso-PMSAS and PMSAP. The compoud PMSATen indicates two peaks at 1380 and 1370 cm^{-1} due to $C(CH_3)_2$ groups contributed from diamine. A strong band is observed in the Schiff base polymers within 1275-70 cm^{-1} due to phenolic C-O bond vibration [9.11].

The band observed around 1630 cm^{-1} in PMSATen, dl-PMSAS and meso-PMSAS shift -10cm^{-1} in copper(II) and nickel(II) coordination polymers and is observed at 1620 cm^{-1} [10], follwoed by a shoulder around 1605 cm^{-1}. The nickel(II) and copper(II) polychelates also indciate bands within 1535-30 cm^{-1} and 1470 cm^{-1}. The shifts in band position in polychelates as compared to Schiff base polymers may be attributed to coordination with metal ions. A number of bands are observed within 900-650 cm^{-1} due to out of plane C-H vibrations, characteristics of adjacent aromatic hydrogen atoms in all the compounds. Comparing the IR spectra of the Schiff base polymers and their polychelates a band is observed in copper and nickel polychelates within 460-5?0 nm, which could be due to metal ligand vibrations [8].

A number of spectrophotometric studies have been reported on monomeric Schiff bases and their metal derivatives [19,20], but a few are available on polymeric Schiff bases and their metal derivatives [10]. The spectrophotometric studies of PMSATen, dl-PMSAS and meso-PMSAS were carried out in THF and PMSAP and copper and nickel polychelates were carried out in DMSO (table 2). The polymeric Schiff bases indicate two to four bands within 380-240 nm. The compounds dl-PMSAS and meso-PMSAs indicate a band at 241 nm and compounds dl-PMSAS, meso-PMSAS and PMSATen indicate a band within 254-258 nm. However PMSAP indicate a similar band at 260 nm in DMSO. The band could be assigned to π-π* transition in benzoid rings and C=N groups [18, 21]. A band is observed within 329-335 nm in all the four Schiff base polymers. A similar band has been assigned to π-π* transition in conjugated azomethine [22]. The compound PMSAP also indicate bands at 288 nm and 380 nm in DMSO. The former band may be due to intra ligand π-π* transition, but the latter is of lower relative intensity and may have origin from n-π* transition,

The copper(II) and nickel(II) polychelates indicate four to five bands within 258-565 nm. All the polychelates indicate a band within 258-65 nm and PMSATenCu, dl-PMSASCu, meso-PMSASCu and dl-PMSASNi indicate also band within 278-288 nm. The band may be due to π-π* transitions in benzoid rings. Their position slightly different than Schiff base polymers may be due to better coordination with metal ions. The copper(II) polychelates indicate a band within 375-80 nm, but corresponding band in nickel compounds is observed within 330-350 nm due to intra ligand π-π* transition as for ligands. The nickel compounds

TABLE - 2

SPECTROPHOTOMETRIC DATA OF SCHIFF BASE POLYMERS AND THEIR METAL CHELATES

NAME OF THE COMPOUND	SOLVENT	REDUCED VISCOSITY	λmax nm (ϵ.1%)
1. meso-PMSAS	THF	0.133	241(386), 285(395) 331(179)
2. dl-PMSAS	THF	0.153	241(356), 256(403) 332(154).
3. PMSATen	THF	0.315	254(284), 329(154)
4. PMSAP	DMSO	-	260(150), 288(56), 335(62), 380(15)
5. meso-PMSASCu	DMSO	-	260(625), 282(396), 380(164), 565(44).
6. meso-PMSASNi	DMSO	-	260(119), 335(24) 442(13), 455(8)
7. dl-PMSASCu	DMSO	-	258(87), 288(46) 380(18), 550(0.6)
8. dl-PMSASNi	DMSO	-	260(71), 288(24), 350(14), 418(6), 460(3).
9. PMSATenCu	DMSO	-	260(812), 278(659), 375(252), 565(58)
10 PMSATenNi	DMSO -	-	265(162), 330(23), 416(12), 445(8).

indicate a band within 416-22 nm, but a corresponding band is not visible in copper(II) compounds. The band may be assigned to charge transfer as reported for nickel(II) chelates of monomeric Schiff bases [20]. The copper polychelates indicate a band within 550-65 nm, but corresponding band in nickel polychelates absorb within 445-65 nm. The bands may be due to d-d transitions.

The reduced viscosities of PMSATen, dl-PMSAS, and meso-PMSAS showed low values (n red 0.135-0.315), but for PMSAP could not be determined because of low solubility in THF and DMSO. Similarly low η_{red} viscosities have been reported for related Schiff bases [9].

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