

Studies on Some Monomeric & Polymeric Schiff Bases Derived from 5-Vinylsalicylaldehyde Derivatives & Their Metal Complexes

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Various polymerizable chelating schiff bases containing different substituents have been prepared from 5-vinylsalicylaldehyde and aniline derivatives. The acid dissociation constants of these monomeric schiff bases have been evaluated spectrophotometrically. Their pK values show that the strength of the hydrogen bond between the *o*-OH group and the azomethine group is related to electronic character of the *p*-substituent on the aniline ring. Homo- and co-polymerization of the chelating monomers with styrene and 4-vinylpyridine lead to covalently bound polymer ligands. The complexing behaviour of the resulting polymers has been also investigated, which is similar to that of the corresponding monomers.

The use of functionalized polymers in numerous applications has recently received considerable attention¹⁻³. A significant role of functionalized polymers is in enhancing the selectivity in the separation of metals. Chelating polymers are of considerable importance due to their inherent advantages over simple ion exchange resins⁴.

The objective of the present work is to prepare functionalized polymers containing chelating groups and to investigate their complexing abilities toward separation of some transition metal ions. Active functionalized polymers prepared by polymerization of monomers containing the desired chelating groups have a broad range of advantages over those prepared by chemical modification technique. The present paper

describes the preparation and studies of numerous chelating schiff base monomers and their polymers.

Materials and Methods

Commercial grade styrene was washed with aqueous NaOH to remove the stabilizer, then with water and dried over anhydrous Na₂SO₄. 4-Vinylpyridine was distilled *in vacuo* immediately before use. All the reaction solvents were purified and dried before use. IR spectra were recorded in KBr on Perkin Elmer 683 and Pye Unicam 1000 infrared spectrophotometers. Elemental microanalysis were carried out using a Perkin Elmer 240 Elemental Analyser. The electronic spectra of the free ligands were measured on a Unicam SP 8000 spectrophotometer. The pH measurements were carried out on an ORION Digital 201 pH -meter.

Table 1 — Analyses and IR Spectra of Monomeric and Polymeric Schiff Bases

Compd	Yield %	m.p. (°C)	Found (Calc.), %			IR, cm ⁻¹				
			C	H	N	ν OH	ν C=O	ν C=N pyr	ν C=N	ν C—O
IIb	94	115	75.4 (75.9)	6.2 (5.9)	5.3 (5.5)	2880			1625	1280
IIc	70.5	161.5	75.2 (75.3)	5.6 (5.4)	5.7 (5.9)	2670			1628	1310
IIId	92	124.5	71.8 (71.9)	5.1 (4.9)	4.9 (5.2)	2820	1682		1615	1295
IIIa	72		75.5 (75.9)	5.7 (5.9)	5.4 (5.5)				1645	1290
IVa	76		88.9 (89.1)	7.6 (7.4)	1.0 (1.1)				1650	1280
IVb	70.5		78.6 (79.2)	6.5 (6.5)	11.3 (11.8)			1670	1625	1282
IIIb	76.5		70.5 (71.9)	5.3 (4.9)	5.3 (5.2)		1680		1640	1280
IVc	74		86.9	7.2	1.2		1675		1625	

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Preparation of monomeric schiff bases

5-Vinylsalicylideneaniline (IIa) was prepared⁵ by stirring a mixture of 5-vinylsalicylaldehyde⁶ (I) and aniline in methanol. The compound was recrystallized from petroleum ether. 5-Vinyl-salicylidene-*p*-methoxyaniline (IIb), 5-vinylsalicylidene-*p*-hydroxyaniline (IIc) and 5-vinylsalicylidene-*p*-carboxyaniline (IId) were prepared using *p*-methoxyaniline, *p*-hydroxyaniline and *p*-carboxyaniline instead of aniline. Their analytical, m.p. and IR data are given in Table 1.

Polymerization of 5-vinylsalicylidene-p-methoxyaniline (IIb): Homopolymerization

A mixture of 0.63 g (22 mmol) of IIb and 10 mg of azobisisobutyronitrile (AIBN) dissolved in 50 ml benzene was refluxed for 2 days. The mixture was poured into methanol under stirring and the precipitate was filtered off. After washing with methanol, the product was dried to get 0.46 g (72% yield) of IIIa, relative viscosity = 0.853 (0.5% DMF, 19°C).

Copolymerization with styrene

A solution of 0.5 g (2 mmol) of IIb, 2.1 g (20 mmol) of purified styrene, and 10 mg of AIBN in 50 ml of benzene was refluxed for 2 days. After pouring the reaction mixture to stirred methanol, the precipitated polymer was filtered off, washed with methanol and dried. The yellow copolymer IVa was obtained in 76% yield (1.96 g), relative viscosity = 0.874 (0.5% DMF, 19°C).

Copolymerization with 4-vinylpyridine

Poly(5-vinylsalicylidene-*p*-methoxyaniline-Co-4-vinylpyridine (IVb) was prepared by the copolymerization of IIb and 4-vinylpyridine in 1:10 ratio as described for IVa using petroleum ether (60-80°C) as the precipitating medium. The copolymer IVb was obtained in 70.5% yield, relative viscosity = 0.844 (0.5% DMF, 19°C).

Polymerization of 5-vinylsalicylidene-p-carboxyaniline (IId): Homopolymerization

The homopolymer IIIb was prepared from the monomer IId, in a similar way as IIIa, in 76.5% yield, relative viscosity = 0.852 (0.5% DMF, 19°C).

Copolymerization with styrene

Poly(5-vinylsalicylidene-*p*-carboxyaniline)-Co-styrene (IVc) was prepared by the copolymerization of IId and styrene in ratio 1:10 as described for IVa. The copolymer IVc was obtained in 74% yield, relative viscosity = 0.871 (0.5% DMF, 19°C).

*Chelation with metal ions:**General batch procedure*

The polymeric chelates were prepared by adding a solution of a definite amount of the transition metal ion (Co²⁺, Ni²⁺, or Cu²⁺) to a certain amount of the desired polymeric schiff base. The mixture was buffered and stirred at room temperature overnight. After filtration, the polymeric chelate was washed several times with a buffer solution to ensure that all the physically adsorbed metal ions were completely run into the filtrate, and then dried.

*Determination of the metal contents:**(a) In the filtrate*

The metal contents of the filtrate and the collected washing solutions resulting from the polymeric chelate preparations, were determined by complexometric titration with 10⁻² M EDTA. Cu(II) was determined with PAN indicator at pH 5, whereas murexide indicator was used for the determination of both Ni(II) and Co(II) at pH 11. Table 2 summarizes the amounts of the metal ions chelated on the polymers as calculated by difference.

(b) On chelating polymers

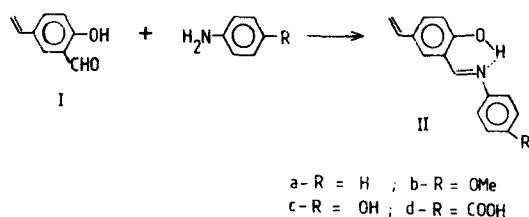
The amounts of metal ions on the chelating polymers were determined by elution with 1N HCl. After carrying out the elution several times, the released metal ions were determined complexometrically (Table 2). Moreover, the results obtained were confirmed by decomposing a definite amount of the polymeric chelate with aqua regia in presence of a small amount of conc. H₂SO₄. The process of decomposition was carried out several times to ensure that all the organic matter was completely destroyed. The released metal ions were also determined by complexometric titration against 10⁻² M EDTA (Table 2).

Table 2—Determination of Metal Ion Contents in polymeric Chelates

Polymer	Polym: Metal (molar ratio)	Metal Contents		
		Cu%	Ni%	Co%
IIIa	2:1	—	—	1.35*
		—	—	(1.02)†
IIIb	2:1	28.64*	—	2.50*
		(28.21)†	—	(2.35)†
IVa	1:1	17.75*	1.50*	—
		(17.53)†	(1.41)†	—
IVb	1:1	49.00*	9.50*	—
		(48.75)†	(9.15)†	—
IVc	3:4	11.25*	—	3.25*
		(10.85)†	—	(3.14)†

* Determined by the elution of the polymer with 1NHCl,

† Determined by the decomposition of the polymer with aqua regia.



Scheme 1

Results and Discussion

The monomeric schiff bases (IIa-d) were prepared by stirring equimolar amounts of 5-vinylsalicylaldehyde (I) with the appropriate aniline derivative in methanol solution (Scheme 1). The structures of the resultant polymerizable compounds were identified by their IR data and elemental microanalyses.

For studying the effect of aniline substituents on the behaviour of the schiff bases (IIa-d), the dissociation constants of these monomers were determined by spectrophotometry. The electronic spectra of IIa in a series of universal buffer solutions covering the pH range 4.85-11.95, are shown in Fig. 1. The λ_{\max} exhibits a red shift as the pH increases which suggests that this band is caused by an intramolecular charge transition from the hydroxyl group. The red shift is caused by the ionization of the *o*-OH group and consequent destruction of the intra-molecular H-bond. The schiff base (IIb) is precipitated in acidic solutions and hence it is impossible to measure its electronic spectra below pH 7. The electronic spectrum of IIb shows a broad band at pH 7 with λ_{\max} at 342 nm, its absorbance decreasing with increasing pH. At higher pH values (8-11.15), a new band appears at 400 nm, whose absorbance increases with increasing pH. A clear isosbestic point is observed at 367 nm indicating the existence of an equilibrium between the ionic form (predominating in solutions of high pH) and nonionic form (predominating in neutral medium).

The spectrum of IIc shows two bands at 345 and 416 nm. The intensity of both bands increases with pH; an isosbestic point is also observed at 455 nm which indicates that a chemical equilibrium exists between ionic species. The spectrum of II d (Fig. 2) also shows two bands at 340 and 400 nm. The intensity of the first band decreases with increasing pH and it disappears above pH 9. The intensity of the second band increases with increasing pH (8.2-11.95), but it disappears below pH 8.2. Three isosbestic points are observed at 325, 330 and 446 nm. However, the absorbance curves at pH 5.2-7.15 deviated from the isosbestic points at 325 and 446 nm. This can be attributed to molecular association probably through intermolecular hydrogen bond of the carboxyl group.

The effect of pH on the electronic spectra of these compounds can be used to evaluate their dissociation

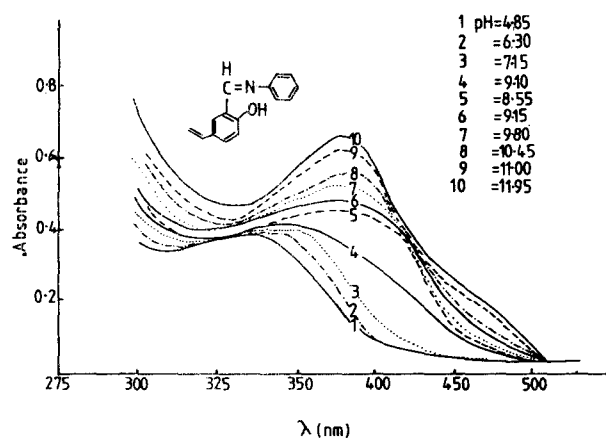


Fig. 1 - Effect of pH on the electronic spectra of $0.8 \times 10^{-4} M$ 5-vinyl-salicylideneaniline.

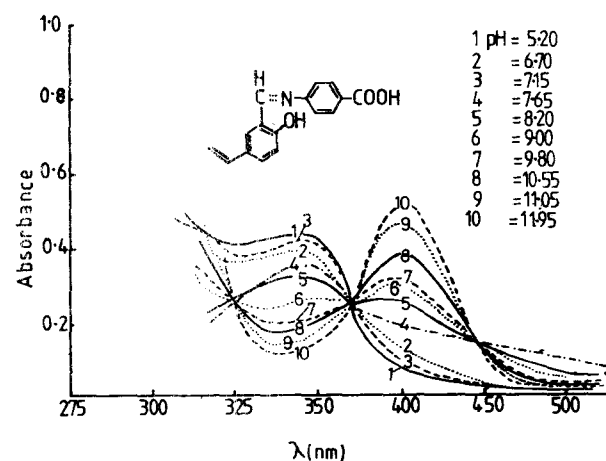


Fig. 2 - Effect of pH on the electronic spectra of $0.8 \times 10^{-5} M$ 5-vinyl salicylidene-*p*-carboxyaniline.

constants, using half-height method (H.H.)⁷, limiting-absorbance method (L.A.)⁸, modified-limiting-absorbance method (M.L.A.)⁷, isoabsorptive-point method (I.P.)⁷, modified-isoabsorptive-point method (M.I.P.)⁷ and Colleter method^{7,9}. From the results given in Table 3, the effect of molecular structure on the *pK* values can be summarized as follows: (i) the *pK* values of IIa-d are lower than those of their analogues without 5-vinyl group. This means that the conjugation property of the olefinic residue facilitates the ionization of the *o*-OH group.

(ii) The electron donor substituents in the *p*-position on the aniline ring decrease the ionization of the *o*-OH group. These substituents increase the strength of the intramolecular hydrogen bond due to increased electron density on the azomethine linkage. This effect can be shown clearly from the decreased ionization constants of *o*-OH groups in the order: H, *p*-OMe, *p*-OH, respectively.

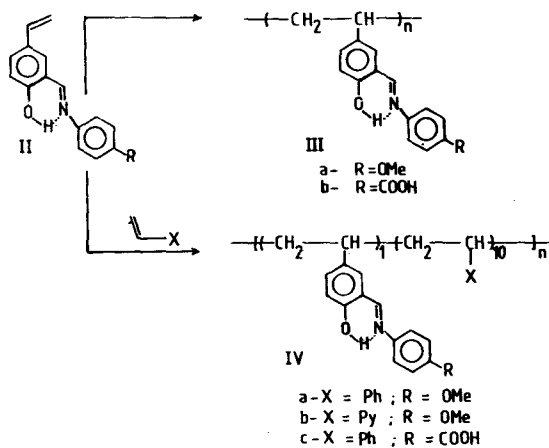
Table 3—The Calculated Values of the Ionization Constants of the Monomers, II

Compd	λ_{\max} (nm)	pK values					
		H.H. method	L.A. method	M.L.A. method	I.P. method	M.I.P. method	Colleter method
Ila	410	820	7.95	8.20			8.32
I Ib	400	8.45	8.10	8.45			8.57
					7.95	8.25	
	345	8.55	9.50	8.55			8.60
I Ic	400	8.10	8.05	8.05			8.14
		10.35	10.18	10.32			10.29
I Id	400	7.72	7.35	7.75			7.63
		10.85		10.75	8.75	7.75	10.69
	350	7.96		8.00	9.30	10.50	7.77
		10.83	9.75	11.05			10.65

(iii) The electron acceptor substituents, such as COOH group, are expected to decrease the pK value of the o -OH group due to the decreased electron density on the C=N group. However, two pK values are obtained for Ila as 7.7 and 10.75, the former value is assigned to the ionization of p -COOH group. This abnormal value indicates that IId exists in an associated form through the formation of intermolecular hydrogen bond. The latter pK value (10.75) is assigned to the ionization of o -OH group in the aldehyde ring. This unexpected value for the ionization of o -OH group indicates that the p -COOH group assists the formation of strong intramolecular hydrogen bond between the o -OH group and the azomethine linkage i.e. the carboxyl group probably behaves as an electron donor once it ionizes through its resonating structure.

The homopolymerization of the monomeric schiff bases (I Ib, d) was carried out by radical initiator, AIBN, in presence of inert solvent to give polymeric schiff bases (IIIa,b) indicating that the phenoxy radical, if formed, did not interfere with the polymerization radical since the phenolic hydrogen is internally hydrogen bonded to the azomethine group. These monomers were also copolymerized with styrene and 4-vinylpyridine in ratio 1:10, as shown in Scheme 2. The structures of these polymeric ligands were identified by elemental analysis and IR spectra (Table 1).

From the results of the metal ions chelated on the polymers (Table 2), it appears that the nature of the chelating groups and the polymer structures have a marked effect on the chelation capacities. Thus, polymers with hydrophilic groups, such as IVb, have higher capacities for chelation than polymers with hydrophobic groups, such as IVa and IVc. Polymers with chelating functional groups bearing p -electron donor substituents (OMe) on the aniline ring, (IVa) and (IVb), show high capacities for chelation with metal



Scheme 2

ions. The electron donor substituents make the azomethine nitrogen stronger coordinating site. However, with p -electron acceptor substituents, such as COOH, the previous effect is expected to be reversed; but high capacities are observed in these cases also, which is attributed to the ease of ionization of carboxyl group. The ionization of this group results in increased compatibility which assists the formation of strong coordinate bond between the metal ion and the azomethine nitrogen and the two effects lead to the observed higher capacities observed for polymers IIIb and IVc. These chelation capacities in polymers are in good agreement with the stability constants of their corresponding monomeric chelates at pH 10 where the polymers show higher chelation for Cu(II) than for Co(II) and Ni(II) as expected from the pK_c measurements.

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