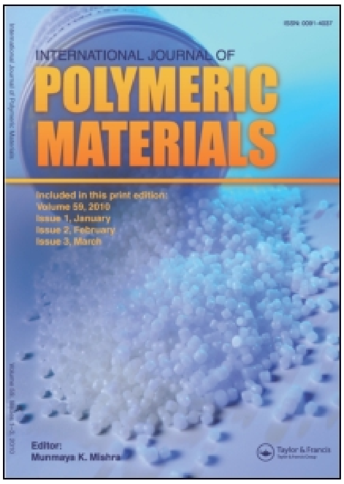

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Synthesis, Characterization and Electrical Conductivity of Polyesters Containing Azomethine Linkages

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The synthesis and characterization of some polyesters containing azomethine linkages are reported here. The electrical conductivity of these polyesters is measured and the results are explained with simple Pariser-Parr-Pople calculations. The polymers are doped with Ag and the electrical conductivity of most of the doped polymers is found to register significant increase. Attempts are made to explain this increase in electrical conductivity.

Keywords: Polyesters; Azomethine; Synthesis; Electrical conductivity

1. INTRODUCTION

Electrical conductivity of organic polymers has drawn attention of many researchers [1–8]. In earlier communications [3, 4, 7], we made attempts to explain the conductivity of organic polymers employing Pariser-Parr-Pople (PPP) molecular orbital (M.O.) theory. The present investigation was carried out in continuation of our work [7] on the synthesis and electrical conductivity polyesters containing azomethine linkage, where use was made of frontier electron density type index to explain conductivity.

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We report here the synthesis, characterization and electrical conductivity of a few new polyesters containing azomethine linkage. These polyesters were doped with Ag when the conductivity increased many fold.

As in the earlier work [7], in this study the conductivity of polymers are explained with frontier electron density type index obtained from simple PPP M.O. calculation.

2. EXPERIMENTAL

2.1. Materials

All the reagents used were of AR grade. The solvents used were purified by standard methods [9].

2.2. Preparation of Monomers and Polyesters

2.2.1. Schiff's Base Monomers

A solution of 0.02 mole of β-hydroxy α-napthaldehyde in 50 ml of absolute alcohol was added slowly to a solution of 0.01 mole of aromatic diamines (*p*-phenylenediamine/benzidine/diaminodiphenylether) dissolved in 100 ml of absolute alcohol through a dropping funnel with constant stirring. The reaction was catalyzed by a few drops of conc. HCl which were added to the aldehyde solution. The contents were refluxed for about two hours. The yellow precipitates obtained were washed with hot R-spirit several times to remove the unreacted material. The Schiff's bases were dried under vacuum. The reaction is depicted in Figure 1.

2.2.2. Polyesters

0.01 mole of Schiff's base was dissolved in about 50 ml of 2 M NaOH. A solution containing slight excess of acid chlorides (of terephthalic acid and isophthalic acid Fig. 2) in 25 ml chloroform (anhydrous) was introduced rapidly with stirring. The stirring was continued for 30 minutes at room temperature in a water bath. The polymers in powder form thus obtained were separated by filtration. All these

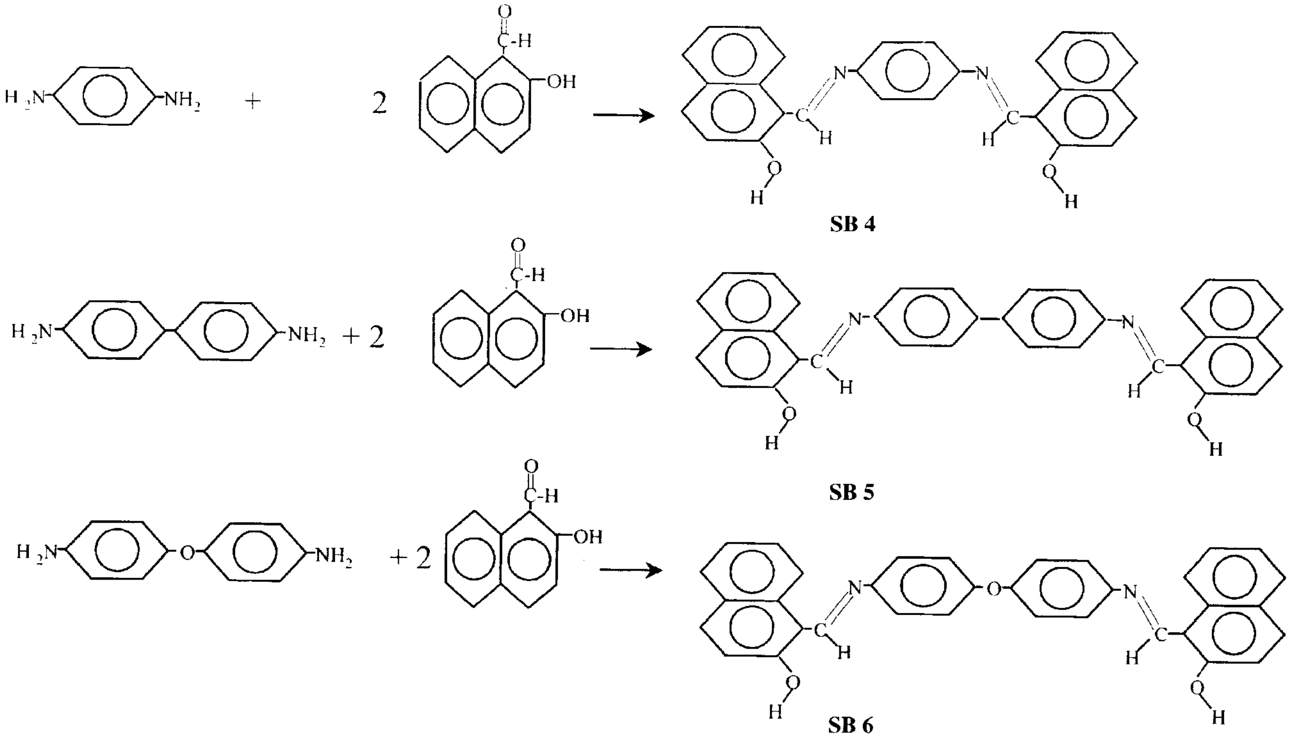

FIGURE 1 Preparation of Schiff's base.

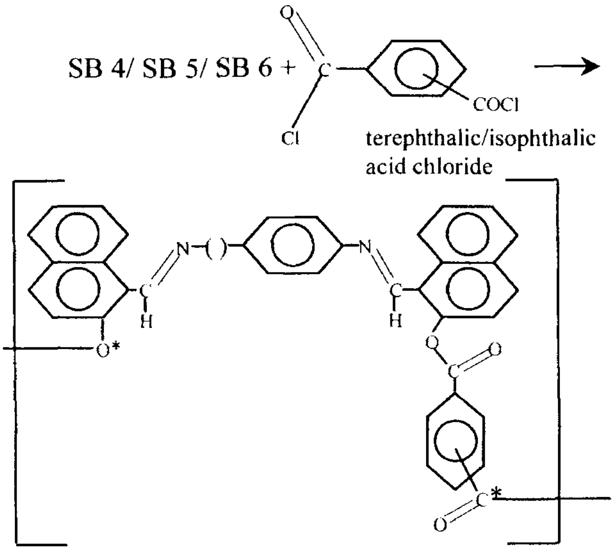

FIGURE 2 Preparation of polyesters.

polymers were washed thoroughly with aqueous sodium bicarbonate solution to remove any acid formed. These polymeric powders were then dried under vacuum for 48 hours.

2.2.3. Doping

Doping is used here in the broadest sense of the word and it is the process of generation and incorporation of atomic species of silver into the polymer matrix. 1 : 1 molar solution of silver nitrate and formaldehyde in DMF was added to the polymer kept in DMF [10]. The mixture was kept in dark for 12 hours. The polymer was then filtered through a fluted filter paper, washed several times with cold double distilled water. The silver doped was estimated by decomposing known amount of the doped polymer with conc. Sulphuric acid – Nitric acid mixture. The silver was precipitated as silver chloride and weighed.

2.2.4. Measurements

The IR Spectra (KBr pellets) were recorded on Perkin Elmer-983 and FT-IR impact 400_D spectrophotometer. Shimadzu UV visible recording spectrophotometer model UV-160 A was employed for recording UV spectra. Conductivity of compressed pellets was measured on Hewlett-Packard high resistance meter 4329A, Kelvin Bridge and Phillips digital multimeter. The carbon, hydrogen and nitrogen were analyzed with Heraeus C H N—O Rapid Analyzer.

3. RESULTS AND DISCUSSION

3.1. Characterization of Monomers and Polymers

The elemental analysis (Tab. I) of monomers and polymers indicated that in each polyester the monomers are practically in equimolar proportions. The partial IR spectral data of monomers (Schiff's base) and the polymers are shown in Table II.

The characteristic carbonyl peak of aldehyde at 1700 cm^{-1} [11] is found absent in the Schiff's bases, while a new strong absorption around 1620 cm^{-1} appears. This is assigned to C=N stretching [12]. The stretching of the OH group at 3425 cm^{-1} remains practically the same in the aldehyde and the Schiff's bases. All the Schiff's bases

TABLE I Elemental analysis of monomers and polymers

		Elemental analysis (%) found (calc.)*	
System	*Carbon*	*Hydrogen*	*Nitrogen*
SB4	79.60	4.78	7.01
	(80.76)	(4.8)	(6.73)
SB5	81.52	4.82	(5.91)
	(82.92)	(4.87)	(5.69)
SB6	79.22	4.68	5.87
	(80.31)	(4.72)	(5.51)
TERSB4	77.56	4.36	5.32
	(78.83)	(4.38)	(5.11)
ISOSB4	77.65	4.35	5.29
	(78.83)	(4.38)	(5.11)
TERSB5	79.83	4.55	4.70
	(80.77)	(4.49)	(4.49)
ISOSB5	79.75	4.53	4.65
	(80.77)	(4.49)	(4.49)
TERSB6	77.22	4.21	4.58
	(78.75)	(4.28)	(4.28)
ISOSB6	77.53	4.42	4.53
	(78.75)	(4.28)	(4.28)

* Values in parentheses are theoretically obtained.

TABLE II Important IR bands (cm^{-1}) of monomers and polymers and their assignments

System	$\nu(OH)$	$\nu(Ar—H)$	$\nu(C=O)$	$\nu(C=N)$	$\delta(C—O(H))$	$\nu(C—O)$
SB4	3400	3050	–	1620	1320	1280
SB5	3400	3050	–	1618	1320	1280
SB6	3400	3050	–	1620	1320	1280
TERSB4	–	3050	1660	1616	–	1290
ISOSB4	–	3050	1660	1615	–	1290
TERSB5	–	3050	1660	1615	–	1290
ISOSB5	–	3050	1660	1615	–	1290
TERSB6	–	3050	1665	1612	–	1290
ISOSB6	–	3050	1660	1610	–	1290

have bands in the region 1500 – 1600 cm^{-1} which may be assigned to aromatic C=C vibrations [11]. Also a band in the region of 3050 cm^{-1} is attributed to aromatic C—H stretching. The same band due to presence of azomethine group in the Schiff's bases is found at 2950 cm^{-1}. The C—O stretching frequency of the C—O(H) moiety in each of the Schiff's bases is found around 1280 cm^{-1} [13]. This in the polymers shift to around 1290 cm^{-1} as the H is replaced by >C=O group. A medium strong band around 1320 cm^{-1} is found in all the Schiff's bases. This band is likely to be associated with bending [13] of phenolic —OH group present at β position of napthalene in each Schiff's base. This phenolic OH bending is absent in the polyesters derived from Schiff's bases with terephthalic and isophthalic acid chloride. Also the —OH stretching absorption in the Schiff's bases at 3425 cm^{-1} becomes extremely weak in the polyester. As expected, in each of the polymers a new absorption around 1660 cm^{-1} due to C=O stretching is observed.

The above discussion supports the structures proposed for these polymers as shown in Figure 2.

It is interesting to note that the intensity of corresponding peaks in the polymers is more than those in monomers, since in polymers more number of similar functional groups are present.

3.2. Pariser Parr Pople M. O. Calculation

3.2.1. Method of Calculation

Like our earlier communications [3, 4, 7], Pariser-Parr-Pople method without configuration interaction was employed to study the polymers, as it is thought that the extent of delocalization of the Π electrons will be the major contributor to the conductivity of these polymers.

The Fock matrix elements within the framework of PPP method are

$$F_{\mu\mu} = u_\mu + 0.5P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\neq\mu}(P_{\nu\nu} - Z_\nu)\gamma_{\mu\nu} \qquad (1)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - 0.5P_{\mu\nu}\gamma_{\mu\nu} \qquad (2)$$

The values of u_{μ} (valence orbital ionization energy) and $\gamma_{\mu\mu}$ (one-center electron repulsion integral) were taken from the literature [14]. Z_{ν} is the core charge. The Nishimoto Mataga expression [15] was employed to calculate $\gamma_{\mu\nu}$, the two center repulsion integral. The value for the resonance integral $\beta_{\mu\nu}$ were taken from comparable molecules and kept same for similar pair of atoms $\mu\nu$ for all the molecules investigated.

The secular equation was solved in the usual way and iteration continue until self-consistency in the bond-order matrix was obtained. The bond lengths and angles of the species were obtained from the literature.

3.2.2. Discussion

The PPP calculation for a complete polymer chain is impossible hence the repeating units of each polymer and the monomers (SB4, SB5, SB6) as shown in Figures 1 and 2 were subjected to PPP calculation.

The mechanism of electrical conduction in polymer may not be a simple one. One of the possible routes may be that electron(s) from HOMO (Highest Occupied Molecular Orbital) of the repeating unit is (are) transferred to the LUMO (Lowest Unoccupied Molecular Orbital) and possibly to the next higher orbital where electron density at certain appropriated place(s) become high, which helps in conduction.

3.2.2.1. Monomers and Polymers It will be worth examining the role of ΔE, the difference in energy of the HOMO and LUMO in the electrical conduction.

The ΔE for the monomers and the repeating units of different polymers is shown in Table III.

The ΔE values of the Schiff's bases are not significantly different from those in polymers. Interestingly, the conductivity of the terephthalic acid polymers has improved considerably over the respective Schiff's bases. However for the isophthalic acid polymers, the increase in conductivity donot appear large. It appears simple correlation between electrical conductivity and ΔE values is not apparent.

TABLE III HOMO, LUMO energies and conductivity of monomers, polymers

	HOMO	*LUMO*	ΔE	*(Frontier*[a] *electron density)*		*Conductivity*
Systems	*(eV)*	*(eV)*	*(eV)*	C^*	O^*	$\Omega^{-1}\ cm^{-1}$
SB4	-8.69	-2.70	5.99			3.9×10^{-14}
SB5	-8.67	-2.69	5.98			1.56×10^{-14}
SB6	-8.88	-2.58	6.30			1.56×10^{-13}
TERSB4	-8.71	-2.94	5.77	0.1105	~ 0	7.8×10^{-9}
ISOSB4	-8.74	-2.77	5.97	0.0047	0.0012	7.8×10^{-10}
TERSB5	-8.69	-2.94	5.75	0.1091	~ 0	3.9×10^{-9}
ISOSB5	-8.72	-2.75	5.97	0.0077	~ 0	7.8×10^{-12}
TERSB6	-8.89	-2.92	5.97	0.1107	~ 0	7.8×10^{-9}
ISOSB6	-8.91	-2.69	6.22	0.0404	0.0002	1.56×10^{-11}

[a] The frontier electron density index at each center is obtained from lowest unoccupied orbital, *i.e.*, the LUMO.

Since no simple correlation is obtained between ΔE and conductivity of the polymers, it was thought appropriate to calculate as was done in our earlier communication [7], the frontier electron density type index (S_r) from the equation

$$S_r = 2\sum c_{ir}^2/k_i \tag{3}$$

at the rth atoms (shown with asterisk in the figures) which connect the repeating units. This index (S_r) has been corrected for electron energy (k_i) of the ith level. It is generally believed that LUMO is important in conduction when the electron is excited from the occupied orbitals. It has generally been accepted that highest occupied molecular orbital (HOMO) forms the valence band while the lowest unoccupied molecular orbital (LUMO) is the conduction band [16]. Consequently S_r in the Eq. (3) was calculated for the orbital LUMO in undoped polymers. The frontier electron density type index at the concerned atoms (C^* and O^*) are shown in Table III.

It is interesting to note that when the electron is excited from HOMO, the terminal atom C^* has an accumulation of electron density (Tab. III). The other terminal atom *i.e.*, O^* has practically very small electron density. So there is flow of electron charge from C^* of one repeating unit to the O^* of other unit. It is logical to expect that conductivity can be correlated to the frontier electron density type index (S_r) at C^* atom. Interestingly a simple correlation is found between the frontier electron density index and the electrical conductivity (Tab. III). All the TER polymers have practically the same conductivity and almost similar S_r value at the C* atom. However for the ISO polymers, no such simple correlation among the different polymers could be obtained. But in each series, the frontier electron density type index (S_r) at C* atom of the ISO polymers is significantly less than the TER polymers and so is the conductivity.

Since the conductivity is a complex phenomenon, where ΔE is also likely to play some role. The value of ΔE for the iso polymers is more than the corresponding TER polymers. This could probably account for the less conductivity of the former. Interestingly, ΔE value for the ISOSB6 is maximum and the frontier electron density type index (S_r) at C* atom for this polymer is more than the said value in other iso polymers. This probably accounts for the comparable conductivity of the ISO polymer.

3.2.2.2. Ag-doped Polymers Doping of the polymers with silver increases the conductivity many fold. Consequently, it becomes necessary to invoke a mechanism to explain such an increase. As has already been discussed, the conductivity is dependent on the electron density at C* in the unoccupied orbitals. Since Ag atom can freely share its electron(s), it maybe that the said electron(s) from Ag is accommodated in different unoccupied orbitals of the concerned polymer. Next question, which comes up, is how many unoccupied orbitals are to be considered! It was thought appropriate to calculate the frontier electron density index S_r at the atom C* and O* considering the two unoccupied orbitals *i.e.*, the LUMO and the one

TABLE IV Frontier electron density index and conductivity in doped polymers

	Frontier electron density[a]			
System	*C**	*O**	*Conductivity* $\Omega^{-1}\,cm^{-1}$	*% Ag*
TERSB4	0.1136	0.0014	8.4×10^{-2}	24.3
ISOSB4	0.1232	0.0015	1.56×10^{-1}	25.5
TERSB5	0.1162	0.0012	1.18×10^{-1}	25.9
ISOSB5	0.1012	0.0016	1.16×10^{-1}	25.2
TERSB6	0.1199	0.00019	3.9×10^{-8}	13.9
ISOSB6	0.0961	0.0013	2.6×10^{-9}	14.6

[a] The frontier electron density at each centre is obtained from LUMO and the unoccupied orbital next to LUMO.

next higher to it. It is likely that these two more stable orbitals *i.e.*, LUMO and the next higher to it, play important role in conductivity of the doped polymer.

Here the conductivity of the doped polymers changes directly with the S_r value at the C* in each polymer (Tab. IV).

The S_r value (at C*) for the ISO polymers show significant improvement when two unoccupied orbitals are considered, but for TER polymers the values do not show appreciable change compared to ones shown in Table III for undoped polymers. It maybe that contribution from other unoccupied orbitals besides these two towards conductivity in doped polymers cannot be just neglected.

The measured conductivity is an aggregate property. It is quite likely that in an assembly of molecules, electrons from silver may be accommodated randomly at different unoccupied orbitals in different molecules of a particular polymer. The observed conductivity of the doped polymers is a result of this random distribution. Here again, the inter series correlation is not possible.

3.3. UV Transitions in Schiff's Base and Polymers

All the Schiff's bases and their polymers show the characteristic $\pi \rightarrow \pi^*$ (Tab. V) transition around 255 nm. The UV spectra of the Ag doped

TABLE V Ultra violet spectral data*

System	$\lambda 1$	$\lambda 2$	$\lambda 3$	$\lambda 4$
SB4	256	301	342	515
SBS	257	301	342	480
SB6	255	–	343	456
TERSB4	257	301	342	–
	(256)	(299)	(343)	–
ISOSB4	251	300	342	360
	(256)	(302)	(343)	–
TERSB5	257	301	342	356
	(257)	(300)	(342)	(480)
ISOSB5	255	–	343	–
	(258)	(301)	(343)	–
TERSB6	250	–	319	–
	(254)	(301)	(344)	–
ISOSB6	250	–	342	360
	(256)	(301)	(343)	(466)

* The values in parentheses are for doped polymers.

polymers do not register any significant change over the respective polymers. This is not unexpected as Ag is not involved in formation of any chemical bond with the polymer, but simply acts as a source of electron donor.

4. CONCLUSION

In comparison to the respective Schiff's bases, the ΔE values (the difference in energy between HOMO and LUMO) for the corresponding polymers did not decrease significantly. This might be one of the reasons why the conductivity of the polymers did not register substantial increase. However, a reasonably good correlation could be obtained between the conductivity of the polymers and the frontier electron density index at C^* atom.

On doping with Ag, the conductivity of the polymers increased many fold. Attempts have been made to explain the conductivity of the doped polymers employing frontier electron density type index obtained from LUMO and some other unoccupied orbitals next to LUMO.

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