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## **Preparations, properties and theoretical studies of a few polyimines containing ester linkages**

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### **ABSTRACT**

*Synthesis and characterization of some polyimines containing ester linkages are reported here. The electrical conductivity of these polymers is measured and the results are explained using quantum mechanical (AM1) as well as molecular mechanical (MM2) calculations. The polymers are then doped with Ag and a few mineral acids. 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:** Polyimines; ester linkages; Synthesis; Electrical conductivity.

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### **INTRODUCTION**

Electrical conductivity of organic polymers has drawn attention of many researchers [1-8]. In earlier communications [7, 8], 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, 8] on the synthesis and electrical conductivity polyesters containing azomethine linkage, where use was made of frontier electron density type index to explain conductivity.

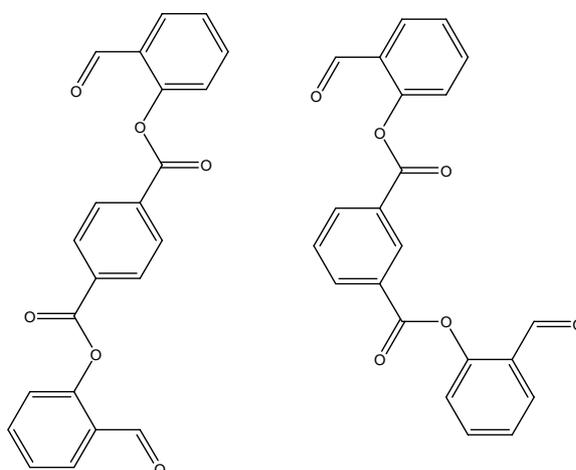
We report here the synthesis, characterization and electrical conductivity of a few polyimines containing ester linkage. These polyesters were doped with Ag and few mineral acids when the conductivity increased to some extent. Alternative to our earlier work [7, 8], in this study the conductivity of polymers are explained with AM1 semi-empirical self consistent field method as well as molecular mechanics.

**EXPERIMENTAL SECTION***Materials*

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

*Preparation of Monomers and Polyimines**Dialdehyde Monomers*

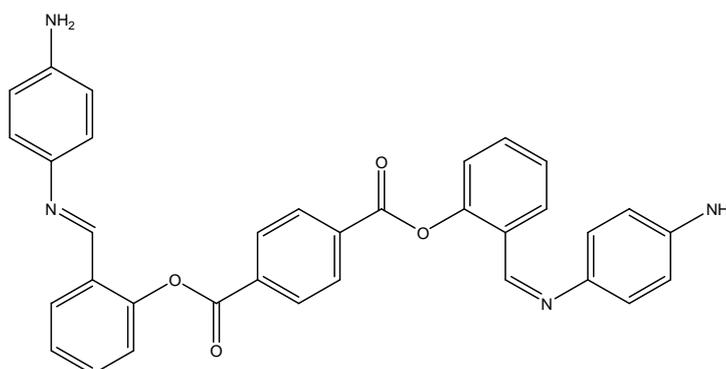
A solution of 0.01 moles of Ter / Isophthaloyl Chloride in 50 ml of absolute alcohol was added slowly to a solution of 0.01 mole of salicylaldehyde dissolved in 50 ml of absolute alcohol through a dropping funnel with constant stirring. The contents were stirred on a magnetic stirrer for about two hours. Precipitates thus obtained were washed thoroughly with aqueous sodium bicarbonate solution to remove any acid formed. These resultant dialdehydes containing ester linkages were then dried under vacuum. Products DIAL1 and DIAL2 are depicted in Figure 1.

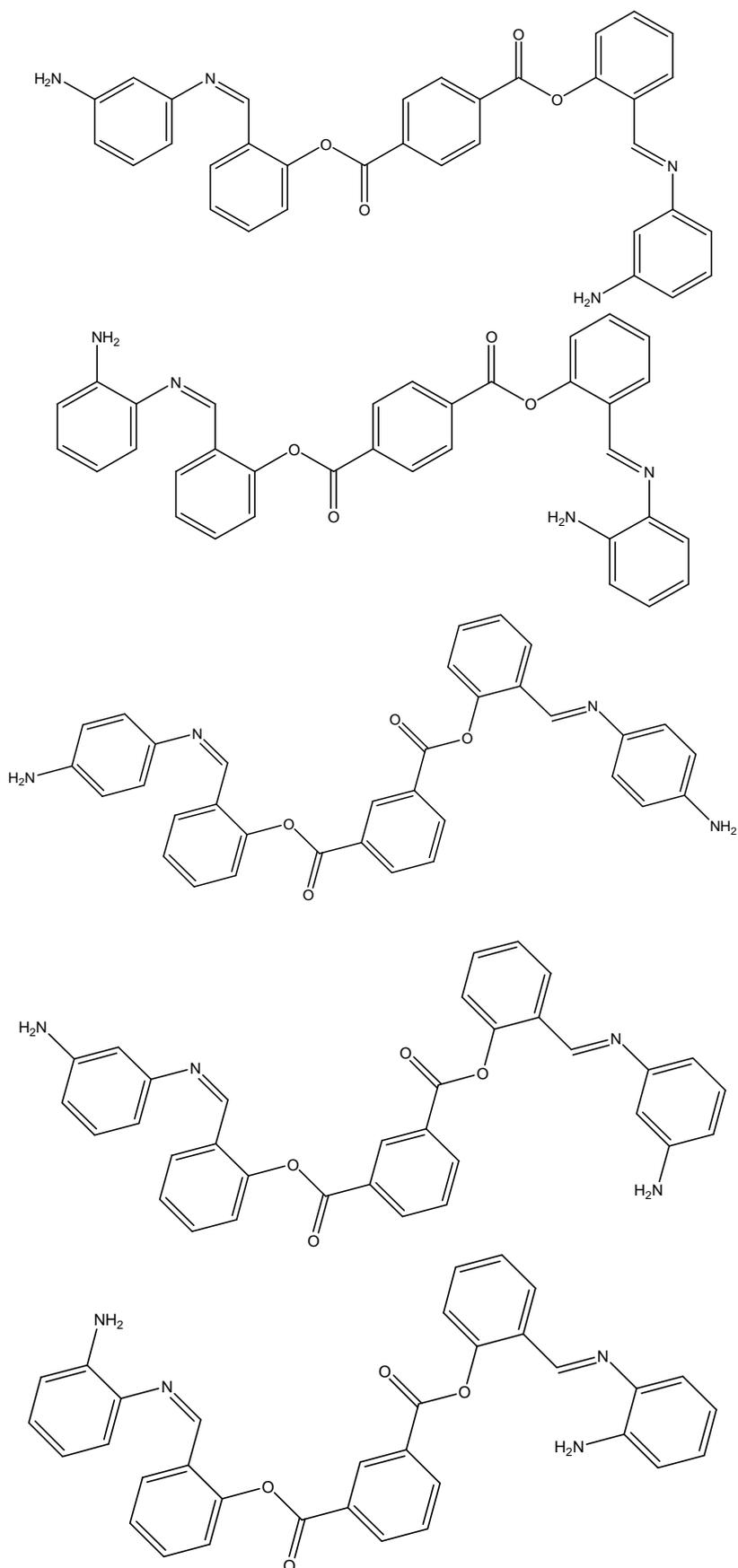


**Figure 1: DIAL1 & DIAL2**

*Polyimines*

0.01 moles of *o*-/*m*-/*p*-phenylenediamine was dissolved in about 50 ml of dimethylformamide (anhydrous). Equimolar solution containing dialdehydes with ester linkages in 50 ml of anhydrous dimethylformamide was introduced slowly with stirring. The stirring was continued for 2 hours at 50 °C in a water bath. The reaction was catalyzed with a few drops of acetic acid. The polymers thus formed were precipitated and were separated by filtration. Precipitates obtained were washed with hot R-spirit several times to remove the unreacted material. These polymeric powders were then dried under vacuum for 48 hours. The structures of the products PI1 to PI6 are shown in figure 2.





**Figure 2: The structures of polyimines containing ester linkages (PolySchiff's bases) PI1 to PI6**

*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 cone. Sulphuric acid-Nitric acid mixture. The silver was precipitated as silver chloride and weighed.

Doping with mineral acids was done by keeping the polymers in 2M acetic acid / hydrochloric acid / sulphuric acid under the influence of ultrasound for 2 hours. The mixture was then allowed to stand for 24 hours and then filtered. Here the terminal amine groups and probably some of the imine groups of the polymer forms adduct with the mineral acids. The polymer was then filtered through a fluted filter paper, washed several times with cold double distilled water.

*Measurements*

The IR Spectra (KBr pellets) were recorded on Perkin Elmer-983 and FT-IR impact 400D spectrophotometer. Shimadzu UV visible recording spectrophotometer model UV-160 A was employed for recording UV spectra. Conductivity of compressed pellets was measured on Solatron Impedance Analyzer Model 260, Kelvin Bridge and Phillips digital multimeter. The carbon, hydrogen and nitrogen were analyzed with Heraeus C H N—O Rapid Analyzer.

**RESULTS AND DISCUSSION***Characterization of Monomers and Polymers**Elemental Analysis*

The elemental analysis (Table 1) of monomers and polymers indicated that in each polymer the monomers are practically in equimolar proportions. Also, the theoretically calculated values of composition are in close agreement with that of the practical ones.

**Table 1 : Elemental analysis of monomers and polymers**

SYSTEM	FOUND (CALCULATED) %		
	CARBON	HYDROGEN	NITROGEN
<b>DIAL1</b>	70.52(70.59)	3.71(3.77)	-(-)
<b>DIAL2</b>	70.15(70.59)	3.75(3.77)	-(-)
<b>PI1</b>	73.12(73.63)	4.72(4.73)	09.95(10.10)
<b>PI2</b>	73.62(73.63)	4.47(4.73)	10.05(10.10)
<b>PI3</b>	72.41(73.63)	4.81(4.73)	09.98(10.10)
<b>PI4</b>	72.92(73.63)	4.69(4.73)	10.12(10.10)
<b>PI5</b>	73.12(73.63)	4.79(4.73)	10.05(10.10)
<b>PI6</b>	72.97(73.63)	4.57(4.73)	10.11(10.10)

*Infrared Spectroscopy*

The partial IR spectral data of monomers and the polyimines (PolySchiff's bases) are shown in Table 2. The stretching of the OH group at 3400  $\text{cm}^{-1}$  remains practically absent in all the dialdehydes and the PolySchiff's bases. A band in the region of 3050  $\text{cm}^{-1}$  observed in both monomers and polymers is attributed to aromatic C—H stretching. Same band due to presence of azomethine group in the PolySchiff's bases is found at 2950  $\text{cm}^{-1}$ . The characteristic carbonyl peak of aldehyde at 1660  $\text{cm}^{-1}$  [11, 14] is found in the monomers which shift to a higher wave number of about 1670  $\text{cm}^{-1}$  is assigned to the carbonyl group of the ester linkage present in the polymers. A new strong absorption around 1620  $\text{cm}^{-1}$  appears in polymers. This band is assigned

to C = N stretching [12, 14]. All the compounds have bands in the region 1500-1600  $\text{cm}^{-1}$  which may be assigned to aromatic C = C vibrations [11, 14]. The C—O stretching frequency of the C—O(H) moiety in each of the monomers is found around 1280  $\text{cm}^{-1}$  [13,14]. This band disappears in case of the polymers.

**Table 2 : Bands Observed in Infrared Spectra of Monomers and Polymers**

SYSTEM	$\nu(\text{OH})$	$\nu(\text{Ar}-\text{H})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{O})$
DIAL1	-	3050	1660	-	2950	1280
DIAL2	-	3050	1660	-	2950	1280
PI1	-	3050	1670	1620	2950	-
PI2	-	3050	1680	1615	2950	-
PI3	-	3050	1670	1620	2950	-
PI4	-	3050	1670	1620	2950	-
PI5	-	3050	1680	1615	2950	-
PI6	-	3050	1670	1620	2950	-

#### *UV Transitions*

All the monomers and their polymers show the characteristic  $\pi \rightarrow \pi^*$  (Table 3) transition around 255 nm. These bands are attributed to the presence aldehyde groups in monomers and imine groups in the polymers [14, 15]. The UV spectra of the Ag doped 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. The spectra of mineral acid doped polymers also did not register any remarkable change.

**Table 3: UV Transitions (nm) Observed in Spectra of Monomers and Polymers**

SYSTEM	A1	A2	A3	A4
DIAL1	257	301	348	-
DIAL2	257	301	342	-
PI1	251	300	343	511
PI2	-	301	342	515
PI3	259	293	342	521
PI4	256	301	346	515
PI5	251	-	342	510
PI6	256	304	345	515

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 is present.

#### *Computational Methods*

##### *Method of Calculation*

In 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 IT electrons will be the major contributor to the conductivity of these polymers.

In the present investigation, we have chosen to employ the AM1 semi-empirical self consistent field method to obtain the energies of the HOMO and LUMO orbitals [16, 17]. This method is an improvised version of modified neglect of differential overlap (MNDO). The wave function here is a closed shell restricted wave function. Spin restrictions allow the Fock matrix to be simplified for a closed shell system. However for an open shell system,  $\frac{1}{2}$  electron approximations

proposed by Dewar are used. Here, unpaired electron is treated as a pair of  $\frac{1}{2}$  electrons with opposite spin.

Since the study involves relatively larger sized molecules, molecular mechanical method (MM2) is also used to understand the electrical conductivity of these polymers [18]. This molecular mechanical method based on laws of classical physics calculates the steric energy of the molecules. It was thought appropriate to calculate the steric energy of one and two repeating units of the polymers for correlating the extent of polymerization with the observed conductivity in the polymers under investigation.

## DISCUSSION

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. Moreover, the extent of polymerization which also depends on the steric factors is expected to show direct proportionality with the electrical conductivity.

### *Monomers and Polymers*

It will be worth examining the role of  $\Delta E$ , the difference in energy of the HOMO and LUMO in the electrical conduction.

**Table 4 Results of AM1, MM2 and conductivity studies of monomers and polymers**

System	Steric energy for one unit	Steric energy for two units	HOMO eV	LUMO eV	$\Delta E$ eV	Conductivity Mho.cm
DIAL1	36.1681	-	-9.76767	-1.45232	11.21999	$6.41 \times 10^{-09}$
DIAL2	36.3341	-	-9.74927	-1.11504	10.86431	$1.32 \times 10^{-09}$
PI1	31.0151	61.4705	-8.04195	-1.10733	09.14928	$5.14 \times 10^{-08}$
PI2	28.9753	51.1347	-8.26048	-1.13022	09.39070	$3.22 \times 10^{-08}$
PI3	29.2550	657.8315	-8.05443	-1.17808	09.23251	$9.72 \times 10^{-09}$
PI4	22.6380	138.8710	-8.10552	-1.07976	09.18528	$6.72 \times 10^{-09}$
PI5	25.8499	50.2786	-8.28932	-1.13448	09.42380	$4.14 \times 10^{-08}$
PI6	26.1189	52.6442	-8.09133	-1.13010	09.22143	$2.65 \times 10^{-08}$

From the Table 4, it is apparent that the electronic conductivity of the molecules increases proportionately with decreasing  $\Delta E$  values. Thus, a simple correlation is observed between electrical conductivity and  $\Delta E$  in the present investigation.

Differences in conductivity observed within a series of polymers needs to be explained using molecular mechanical method. The steric energy calculated for single repeating units is practically indistinguishable across the series. Hence, it is difficult to correlate the conductivity of the polymers with steric energy for single repeating units. Due to this, it was thought appropriate to calculate the steric energy for two repeating units. Interestingly, these values for the polymers PI3 and PI4 are very large which can probably explain the low electrical conductivity in these polymers. The polymer PI3 has ortho, ortho, para, ortho and ortho substituted moieties connected in the series in the chain. In case of PI4, para, ortho, meta, ortho and para substituted moieties connected in the series. The molecular mechanical studies have revealed that the steric energy of such kind of chain will be extremely high. Thus, it is thought that nothing more than oligomers would have resulted from the reaction of the above mentioned

monomers. We propose that the low conductivity in the said moieties is due to very low degree of polymerization.

#### *Doped Polymers*

The conductivity values of the doped polymers are shown in Table 5. Doping of the polymers with silver increases the conductivity by around ten folds. 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 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. Here the conductivity of all the Ag doped polymers show significant improvement.

**Table 5 Electrical conductivities of doped polymers**

Ag doping	Conductivity Mho.cm	Acetate doping	Conductivity Mho.cm	Chloride doping	Conductivity Mho.cm	Sulphate doping	Conductivity Mho.cm
PI1	$1.43 \times 10^{-07}$	PI1	$7.21 \times 10^{-08}$	PI1	$7.14 \times 10^{-08}$	PI1	$5.14 \times 10^{-08}$
PI2	$2.12 \times 10^{-07}$	PI2	$6.32 \times 10^{-08}$	PI2	$6.21 \times 10^{-08}$	PI2	$4.52 \times 10^{-08}$
PI3	$4.02 \times 10^{-08}$	PI3	$2.10 \times 10^{-08}$	PI3	$1.52 \times 10^{-08}$	PI3	$1.11 \times 10^{-08}$
PI4	$3.92 \times 10^{-08}$	PI4	$1.73 \times 10^{-08}$	PI4	$1.24 \times 10^{-08}$	PI4	$1.20 \times 10^{-08}$
PI5	$1.14 \times 10^{-07}$	PI5	$6.31 \times 10^{-08}$	PI5	$5.51 \times 10^{-08}$	PI5	$5.21 \times 10^{-08}$
PI6	$9.75 \times 10^{-08}$	PI6	$6.47 \times 10^{-08}$	PI6	$5.83 \times 10^{-08}$	PI6	$5.15 \times 10^{-08}$

Doping of the polymers by mineral acids has shown an extremely small yet consistent improvement in the electrical conductivity. Here, it is thought that some of the mineral acid molecules might have formed adduct with the terminal  $-NH_2$  groups of the polymer chain. However, no comprehensible mechanism for explaining this increase in conductivity could be thought.

### CONCLUSION

In comparison to the respective monomers bases, the  $\Delta E$  values (the difference in energy between HOMO and LUMO) for the corresponding polymers showed a small decrease. 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 steric energy for two repeating units.

On doping with Ag, the conductivity of the polymers increased around tenfold. Mineral acids could not effect a large improvement in the electrical conductivity of the polyimines. Attempts have been made to explain the conductivity of the doped polymers employing both quantum mechanical and molecular mechanical methods.

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