

## **Effect of Aromatic Ester Groups on Electrical Conductivity of Polyazomethine**

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### **ABSTRACT**

Four types of copolymer have been prepared by solution condensation polymerization of azomethine monomer with four different types of acid chloride (phthaloyl, isophthaloyl, terephthaloyl and fumaryl).

The electrical conductivity of the copolymers have been enhanced by many order of magnitude according to polyazomethine or polyester. The ester group increased the electrical conductivity via two manners, increasing the flexibility of the chain, and making the charge carrier movement more easily along the chain.

The effect of temperature and doping with iodine on conductivity have been investigated. It was found that the electrical conductivity of these types of polymers is deffected by the distortion of the phenyl ring and the flexibility of the chain.

*Key words:* electrical conductivity, polyazomethine, polyester.

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### **INTRODUCTION**

Conducting polymers have unusual properties of possessing high electrical conductivity, and can exhibit a range of properties from semi conducting to near-metallic behaviour. Most electrically-conducting polymers possess an extended conjugated skeleton, which is believed to be not only a basic condition for electrical conductivity but

it is also a major cause of the characteristic intractability and poor mechanical properties of these macromolecules. The progress has been made in enhancing the processibility of these polymers by synthesizing these conjugated polymers via precursor polymer or by attaching solubilizing substituents (Antron et al., 1968).

The electrical properties of aromatic polyazomethines have been studied when doping by iodine and bromine (Kato et al., 1988). Definite structures were incorporated in the chains backbone in order to study the effect of molecular structure on the electronic, physical and electrical properties of the polymer (Yang and Jenekhe, 1995).

The dependence of electrical conductivity on the conjugation length in a polymer is an important topic and has been approached in different ways by various authors (Yang and Karaz, 1994). The short conjugated chains are considered to be dopable and consequently conducting (Masse et al., 1989). It is conceivable that linking conjugated macromolecules block with non-conjugated flexible molecular chains will provide improved system (Yang and Karaz, 1994).

Our approach to this problem is to link short conjugated segments having azomethine structures with segments having aromatic ester group. These two components are dopable with iodine and having different electrical conductivity characteristics. We believed that the ring distortions in the polymer chain will affect the electrical conductivity to some extent. Using of different substituted aromatic ester segments may enhance this idea.

### **Experimental:**

All chemical have been purified according to conventional method (Perrin and Amarego, 1980).

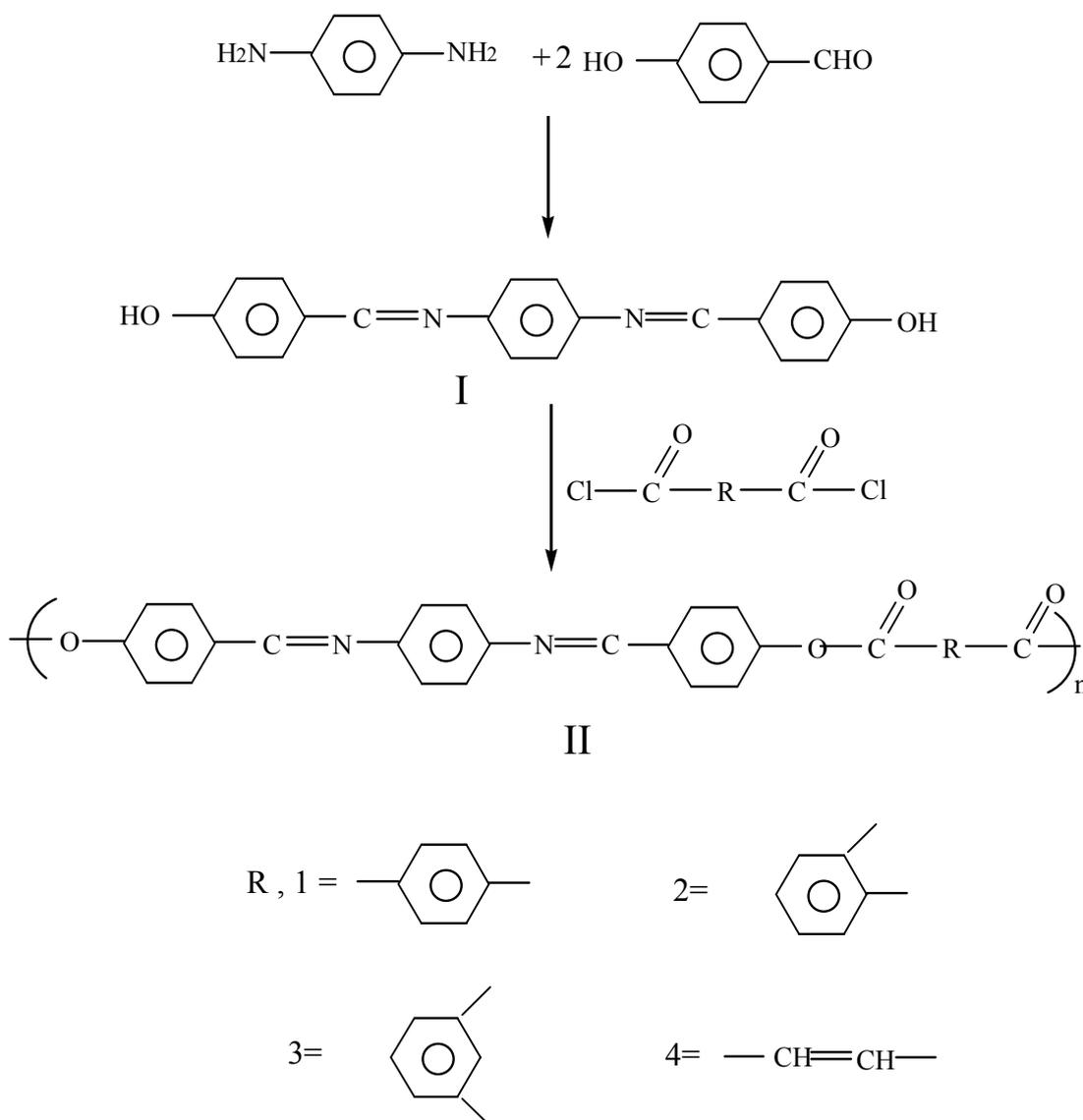
Terephthaloyl dichloride (TDC) was prepared by refluxing terephthalic acid with excess thionyl chloride in presence of a few drops of dimethyl formamide. Phthaloyl dichloride and isophthaloyl dichloride were prepared by the same procedure.

### **Synthesis of the azomethine monomer (*p*-hydroxybenzilidene)-*p*-phenylene diamine): I:**

Two moles of *p*-hydroxybenzaldehyde are mixed with one mole of *p*-phenylenediamine thoroughly in benzene solvent for five minutes, a yellow precipitate is formed.

### **Preparation of polymer II**

Four polymers are prepared by using solution polymerization method (Gadoge et al., 1989) by the reaction of azomethine monomer with an equimolar quantities of acid chloride monomers. The scheme of the reaction is as below:



F.T.I.R. spectra of the azomethine monomer and the related polymers were taken on an Tensor 27 Co.Brucker (FT.IR) Spectrophotometer using KBr disk

#### Doping and electrical conductivity measurements:

Films of (2)cm diameter and (0.6-0.8)cm thicknees from the synthesized polymers were prepared under (3) ton/cm<sup>2</sup> pressure. The films were doped with iodine by exposing the pellet specimens to iodine vapour for different periods at room temperature. The higher dopings levels was achieved by mixing the polymer with different molar ratio of iodine according to repeating unit of the polymer at room temperature .

Volume electrical conductivities were measured by using standard three-probe electrical cell method (ASTM, 1981) .

#### Theoretical measerment:

Theoretical measurements of the bonds length and angles were performed by using CS Chem. Office ultra 60 program for the prepared polymers.

### Results and Discussion:

The synthesis of azomethine monomer is fairly straight forward, the melting point is about 260 °C.

F.T.I.R. spectra of the monomer give the relevant assignment as shown in Table (1).

Table 1: F.T.I.R. spectra of the azomethine monomer.

Absorption / $\text{cm}^{-1}$	Absorbing group
1602,1580,1521,1411	Aromatic C = C st.
1241,839,993	Aromatic C – H def.
1172	C – O st. of phenol
1648,1445	C = N str.

Whereby the spectra of the prepared polymers show another absorption bands appeared at  $(1780 - 1800)\text{cm}^{-1}$ .

The electrical volume conductivity measurement of the prepared polymers have been done at room temperature. The numerical values ( $\sigma$ ) are listed in Table (2).

Table 2: Room Temperature electrical conductivities of the polymers.

4	3	2	1	polymer
$3.93 \times 10^{-7}$	$1.59 \times 10^{-10}$	$2.01 \times 10^{-7}$	$4.25 \times 10^{-10}$	$\sigma / \text{ohm}^{-1}.\text{cm}^{-1}$

The data showed an enhancing in conductivity via polyester ( $\sigma \simeq 10^{-11} \text{ohm}^{-1}.\text{cm}^{-1}$ ) (Shahab and Khattab, 2001) or polyazomethine ( $\sigma \simeq 10^{-14} \text{ohm}^{-1}.\text{cm}^{-1}$ ) (Shkiel et al., 2004) by many order of magnitude. In our opinion, this phenomenon may be explained by two manners, firstly: the ester group with unshared pair of electrons can lead to a molecular association with the azomethine group among the chain, this will enhance the movement of the charge carriers through the polymer chain and increasing conductivity. Second : it was known that the azomethine segments is a rigid, the flexibility can be improved by coupling with an ester group and enhancing the conductivity by increasing the flexibility of the polymer chain (Allock et al., 2003) .

Figure (1) showed a theoretical measurements of the bond lengths and bond angles of phenyl rings in ester segments of the investigated polymers. The bond length of the azomethine group did not changes within the significant observation when attached to ester groups. The results explain that the distortion in the rings exhibit different displacements and take the following sequence:

$$\text{ortho} > \text{para} > \text{meta}$$

These results are compatible with the difference in conductivity of the related polymers.

A theoretical calculations show that ring distortion did not affect the overall

conjugation length (Almenning et al., 1985) but there should be significant coupling to the electronic degrees of freedom (Mao et al., 1993). The more distortion of the ring may decrease the ability of crystal formation within the polymer chain and the amorphous phase is the dominant, leading to increase in the conductivity. Polymer 4 with a vinyl group in ester part had a higher conductivity than other polymers, whereas the overlapping of electrons through the vinyl group are more easily than through aromatic ring.

The results can also be explained by the influence of the electronic factors (resonance and inductive effect) on conductivity. The resonance of aromatic ring provides a reasonable explanation for increasing the conductivity via enhancing the conjugation of the polymeric chains. The conductivity process is affected through transport of charge carriers which is transferred through the space separating the azomethine and ester groups in the polymeric chains (inductive effect).

The surprising high level of conductivity of polymer 2 in comparing with that of polymer 1 and 3 can be rationalized in terms of the above two factors; whereby the azomethine and ester groups are very close to each other, this will enhance the conductivity in participation of resonance effect of the benzene ring. On the other hand, the conductivity of polymer 1, with para linkage in aromatic ring, was decreased, whereby there is a low influence of inductive effect between the azomethine and ester groups, as they are far away from each other. In this case the resonance effect is dominant. The lowest conductivity of polymer 3, with meta linkage in aromatic ring, can be rationalized in terms of the absence of resonance in benzene ring and only the inductive factor is effective but with less sensitive than in polymer 2.

### Temperature effect:

The effect of temperature on conductivity is shown in Table 3.

Table 3: Effect of temperature on the electrical conductivity of the polymers.

$\Delta E / \text{e.v.}$	$\sigma / \text{ohm}^{-1} \cdot \text{cm}^{-1}$	T / K <sup>o</sup>	Polymer
1	$4.25 \times 10^{-10}$	298	0.117
	$6.05 \times 10^{-10}$	323	
	$7.10 \times 10^{-10}$	343	
	$9.07 \times 10^{-10}$	373	
2	$2.01 \times 10^{-7}$	298	0.135
	$2.23 \times 10^{-7}$	313	
	$2.41 \times 10^{-7}$	323	
	$2.95 \times 10^{-7}$	333	
	$3.62 \times 10^{-7}$	353	
3	$1.59 \times 10^{-10}$	303	0.087
	$1.919 \times 10^{-10}$	313	
	$2.15 \times 10^{-10}$	323	
	$2.50 \times 10^{-10}$	343	
4	$3.93 \times 10^{-7}$	293	0.189
	$9.21 \times 10^{-7}$	323	
	$1.26 \times 10^{-6}$	343	
	$1.47 \times 10^{-6}$	353	

The table shows that increasing the temperature is followed by an increasing in electrical conductivity.

According to Serin et al. (2004) increasing the temperature is accompanied by a gradual rise in the population of electrons in conduction band and increasing conductivity. The present effect of temperature can be estimated by calculating activation energy. The activation energy for coloured compound lies between (1.5-2) eV. mol<sup>-1</sup>. Comparing the activation energies for our studied polymers which showed very low and far from the electronic excitation energies and maintain the order:

$$\text{Ortho(1)} > \text{para(2)} > \text{meta(3)}$$

This is the same sequence of the distortion in the benzene rings, where we can see that the activation energy is most likely belong to ring distortion. The activation energy of polymer 4 is higher than the others. This can be explained by that polymer 4 with a vinyl group has a more flexible chain than the other polymer. In this case the activation energy may belong to chain flexibility (Shahab and Khattab, 2001)

### Doping effect:

The prepared polymers are a class of conjugated polymers, that become electrically conductive upon the addition of electron donors or acceptors (doping). The electrical conductivity of the prepared polymers was investigated by using iodine doping agents. The doping procedure is accomplished by exposing the specimen films of the polymers to the vapour of iodine for different times.

The kinetics of doping exhibit a strong dependence of the doping time. As the reaction proceeds, the color of the polymer film changes from a pristine orange to dark red.

The higher conductivity obtained may be due to the easier diffusion of the dopant into the polymer matrix. Table (4) shows the increasing in conductivity of the polymer which is within a consequence of doping by iodine

Table 4: Room temperature electrical conductivities of the prepared polymers doped with different mole ratio of iodine.

Polymer 4		Polymer 3		Polymer 2		Polymer 1	
$\sigma/\text{ohm}^{-1}.\text{cm}^{-1}$	I <sub>2</sub>						
$3.93 \times 10^{-7}$	0	$1.59 \times 10^{-10}$	0	$2.01 \times 10^{-7}$	0	$4.25 \times 10^{-10}$	0
$1.35 \times 10^{-6}$	0.15	$2.0 \times 10^{-8}$	0.05	$1.03 \times 10^{-6}$	0.1	$1.11 \times 10^{-9}$	0.1
$1.45 \times 10^{-6}$	0.2	$2.5 \times 10^{-8}$	0.1	$1.6 \times 10^{-6}$	0.2	$2.28 \times 10^{-9}$	0.2
$2.17 \times 10^{-6}$	0.3	$3.0 \times 10^{-8}$	0.15	$5.6 \times 10^{-6}$	0.3	$4.25 \times 10^{-9}$	0.3
$1.9 \times 10^{-6}$	0.4	$3.5 \times 10^{-8}$	0.2			$7.5 \times 10^{-9}$	0.5
		$4.9 \times 10^{-8}$	0.35				
		$8.9 \times 10^{-8}$	0.5				

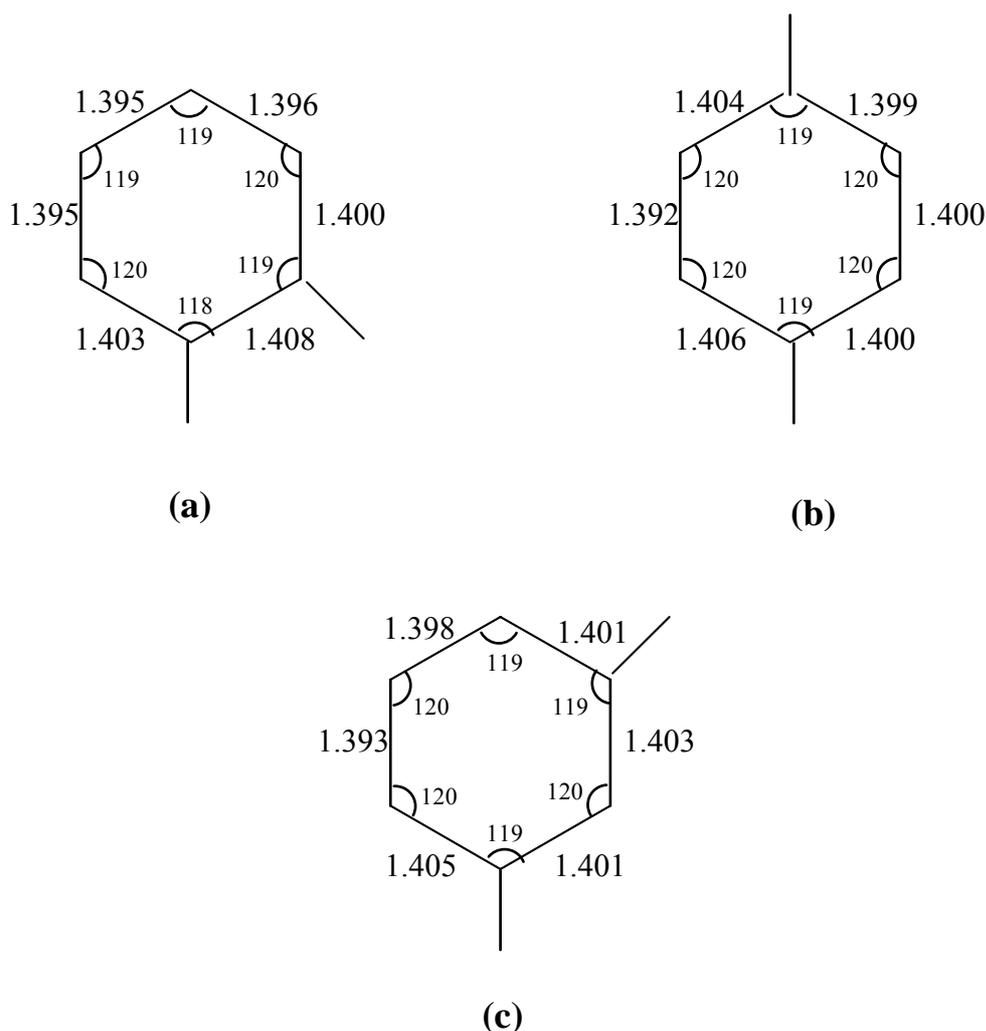


Fig. 1: Theoretical measurements of bond lengths and bond angles of phenyl rings in ester segments (a=ortho substituted, b= para substituted, c= meta substituted)

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